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The Temperature Dependence of the Drying of Horizontal Soil Columns

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THE TEMPERATURE DEPENDENCE OF THE DRYING OF HORIZONTAL SOIL COLUMNS

by

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INTRODUCTION

A consideration of the physical principles involved in evaporative drying of soil indicates that several physical processes might possibly limit the rate of evaporation. These include the rate of supply of energy to the site of evaporation, the rate of transfer of water vapor through the sample or through the atmosphere above the sample, and the rate of unsaturated flow of water to the soil surface or to the site of evaporation.

The objective of the present study has been to gain evidence on the rate limiting process in the evaporation of moisture from soil by studying: (a) the kinetics of the process, (b) the rate of evaporation as a function of the moisture distribution in the soil, and (c) the temperature distribution resulting from evaporative cooling in relation to the rate of evaporation. This objective has been sought through a laboratory study of the non-steady evaporation of moisture from soil columns of high initial moisture content.

The field problem to which the results of the present study are most directly applicable is that of evaporation from fallow soil.

REVIEW OF LITERATURE

Theory of Evaporation

Two fundamental transfer processes are involved in evaporation: (a) the transfer of energy (heat) to bring about the evaporation of the water and (b) the transfer of mass (water) as liquid and vapor within the drying medium and as vapor away from the sample.

Transfer of heat

The limiting cases of evaporation are associated with the temperature of the surface relative to the air a short distance from the surface. The temperature of the surface depends in turn on the method and magnitude of supply of energy to the evaporating surface. On the one extreme the energy supply to the surface is by incident radiation. In the field it is by shortwave solar radiation. The incident radiation heats the surface. Hereafter evaporation will be referred to as "radiation" or "insolation" evaporation whenever the temperature of the surface of evaporation is $\geq$ that of the air a short distance from the surface.

At night and during periods of overcast and cloudy weather or in the shade radiation is restricted and the temperature of the soil may drop below that of the air because of long wave back radiation or evaporative cooling. In this case evaporation from the surface results in the temperature of the surface being $\leq$ that of the air a short distance from the surface. Because the principles of wet-bulb psychrometry (Carrier, 1921) are based on this case, it will be referred to as the "wet-bulb evaporation case" and the accompanying evaporation process as "wet-bulb"

evaporation. The wet-bulb case cannot be referred to as the "evaporative cooling" case unambiguously since evaporative cooling accompanies both cases.

The wet-bulb case applies to most types of artificial drying including kiln drying and vacuum drying. Transpiration from plants may be either radiative or wet-bulb type evaporation depending upon predominant source of energy and availability of moisture for evaporation. Most practical cases are not purely one limiting case or the other because conduction and radiation of heat occurs from container walls or from the medium itself. The direction of deviation of the surface temperature from that of the surrounding air determines the kind of evaporation.

Equality of temperature of the evaporating surface and of the air is a very special case requiring the addition of energy at the evaporating surface from some source other than the air at precisely the same rate that it is used by the latent heat of vaporization and by long wave radiation. The rate of evaporation is directly proportional to the wet-bulb depression when the evaporating surface is at the wet-bulb temperature (Carrier, 1921; Leighly, 1937).

Van den Honert (1948) points out that

> In hygrometric determinations, the temperature difference between the wet and dry thermometer causes a decrease of the saturated vapor pressure at the surface of the wet-bulb corresponding to about 3/5 of the saturation deficit of the air. This means that the evaporation rate is roughly 2/5 of the [hypothetical] isothermal evaporation rate at air temperature....

The existence of the wet-bulb and insolation evaporation cases seems to be a direct consequence of the low heat conductivity and heat capacity of the air (van den Honert, 1948).

Transfer of mass

In both limiting evaporation cases the transfer of water vapor away from the surface is governed by the same principles. There is a thin layer of air in contact with the surface in which laminar flow occurs; this layer grades into a turbulent air layer at a distance from the surface which depends upon windspeed (Leighly, 1937; Anderson, Anderson, and Marciano, 1950). According to Anderson et al. (1950):

> In the laminar layer, of the order of several millimeters in thickness, temperature, humidity, and windspeed vary linearly with height, to a very high degree of approximation. Transfer of heat, of water vapor, and of momentum through this layer are essentially molecular processes and, mathematically, can be handled by classical procedures. In the turbulent boundary layer, windspeed, water vapor, and, to a lesser degree of certainity although to a high degree of approximation, temperature, vary linearly with the logarithm of height. Transfer of heat, of water vapor, and of momentum through this layer are essentially turbulent processes. The thickness of this layer is directly proportional to the degree of turbulence prevailing.

The gradients of water vapor concentration and temperature are much steeper in the laminar than in the turbulent layer. The diffusion coefficient of water vapor in the turbulent layer is roughly 1000 times its value in the laminar layer (Cermak and Spengos, 1956, as reported by Staley[1], p. 59.)

Evaporation equations

The phenomena of evaporation are of wide interest--ranging from calculation of mass transfer and aerodynamic heat transfer for a vaporizing surface in supersonic flight (Bauer and Zlotnik, 1958) to estima-

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[1]Staley, R. W. 1957. Effect of depth of water table on evaporation from fine sand. M. S. Thesis. Colorado State University. Ft. Collins, Colorado

tion of transpiration by insects (Buxton, 1931; Edney, 1957)—and many have sought to state them mathematically.

Dalton law.--Dalton (1802) made the first attempt to express the "true theory of evaporation." After having studied the evaporation of water into air he concluded that "the evaporating force is equal to the vapor tension [at the surface of the water] at the temperature of the water, diminished by that [in the air] at the temperature of the air."[2]

The Dalton law in general form is

$$E = K (p_w - p_a) \qquad (1)$$

wherein E is the rate of evaporation of water,

p_w is the partial vapor pressure of water at the evaporating surface at the temperature of the surface,

p_a is the "ambient vapor pressure of water in air near the surface" (Lowry, 1956) and

K is a proportionality "constant".

The limitations of the Dalton law include those pointed out by Carrier (1921):

> This law holds only for free liquid surfaces or for vapor pressures of the liquid at the surface of a wet material.
>
> It holds only for like conditions of relative atmospheric movement with respect to velocity and direction.
>
> It holds only when the total pressure is greater than the vapor pressure of the liquid.

Carrier's statements should be remembered.

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[2]The insertions are made to clarify the statement so that the accompanying new formulation of the Dalton law will be clear.

Saturation deficit law.—Biologists employ a "saturation deficit" law and express it (Edney, 1957) as

$$E = K (p_o - p_a)$$

wherein E and K are defined as in equation (1),

p_o is the "partial pressure of water vapor in air saturated at the temperature of the surface", and

p_a is the "partial pressure of water vapor in air a short distance away from the surface."

As expressed in equations (1) and (2) the saturation deficit law and the Dalton law differ in two respects, the space reference and the saturation reference. In the saturation deficit law both p_o and p_a are evaluated for the same location in the air. In the Dalton law expression p_w is at the surface and p_a at a point in the air near the surface. In the Dalton law, p_w and p_a are existing vapor pressures. In the saturation deficit law p_a is the existing vapor pressure and p_o is the vapor pressure that would occur at saturation of the air under existing conditions of temperature and overall pressure.

The Dalton and saturation deficit laws are not very rigorous in that no standard distance between the evaporating surface and the point of measurement in air is specified, and the potential difference is simply a difference in partial pressure of water vapor rather than a gradient of concentration as one anticipates for molecular processes. (The meteorological measure of molecular concentration, absolute humidity—$M L^{-3}$, is proportional to vapor pressure at a given temperature, but the proportionality is not the same at all temperatures.)

The generality of the Dalton and saturation deficit laws is challenged by a consideration not yet mentioned. Since they deal only with the transport of vapor through the air (or other gas or vapor phase), they are based on the assumption that vapor transfer by molecular diffusion is rate limiting. There are other physical processes which could be just as effectively rate controlling as vapor diffusion away from the evaporating surface. These include:

(i) The external supply of energy. Since the dominant energy sink in evaporation is that of the phase transition, the supply of energy to the evaporating medium could limit the evaporation rate by controlling the rate of formation of vapor. If incident radiation is low not much energy is absorbed by the evaporating surface, and if the air is calm little energy is transferred from the air to the evaporating surface. The limiting nature of incident radiation and heat transfer apply to both laboratory and field conditions.

(ii) The thermal transmission properties of the evaporating liquid or of the porous material from which water is evaporating. Thermal transmission properties could be the ultimate controlling factor in the rate of evaporation because evaporation from the surface of any medium (free water, soil, plant leaves, textiles, skin) results in evaporative cooling. A temperature difference between the surface and the interior of the medium is thus established. If the heat capacity and thermal conductivity of the medium are low, little heat will flow even though a steep temperature gradient develops.

(iii) Temperature per se at the evaporating surface. On the molecular level, the vapor pressure (or fugacity) and hence the temperature at

the evaporating surface may be considered the "driving force" in evaporation. This reasoning is supported by knowledge that temperature is related to the kinetic energy of the molecules, and that on the molecular scale it should be a good index of the statistical probability of vaporization.

(iv) The transfer of moisture within the drying medium. The transfer of moisture to the site of evaporation by liquid flow, or to the interface between the evaporating medium and the gas atmosphere as vapor may limit evaporation. Carrier (1921) stated that the Dalton law applies only to wet surfaces, but the application of the law is often to surfaces which are not wet.

(v) The resistance offered by the outer membranes of living organisms. Transpiration from plants is of particular importance in the general evaporation problem. The cuticle of plants is an effective barrier to the loss of moisture. The presence of the cuticle and the complex behavior of pores in it, called stomata, challenge any theory based on the assumption that moisture loss by plants is a unique function of external vapor concentration.

Bigelow (1907) transcribed the expressions for evapotranspiration used by several previous workers into the Dalton law form

$$E = K\,(p_w - p_d)(1 + ck) \qquad (3)$$

in which he defined K and c as "constants", p_w as the "vapor pressure at the water-surface temperature", p_d as the "vapor pressure at the dew-point temperature", and k as windspeed. Upon expressing the results of different workers in the form of equation (3) he found that the predicted rates of evaporation ranged from 0.13 to 0.35 mm hr^{-1}.

Bigelow concluded:

> The agreement is so unsatisfactory as to suggest that the formulas have not a comprehensive form, and that so-called constants determined empirically are in reality variable to a considerable extent.

In summary of the Dalton and saturation deficit laws the following statements can be made:

(i) Confusion has often arisen in evaporation theory terminology both inclusive and exclusive of the Dalton and saturation deficit laws (Leighly, 1937; Lowry, 1956). Apparent sources of confusion have included the difficulty in accurately measuring surface temperature, lack of knowledge of the thickness of the laminar layer for a given set of experimental conditions, failure to realize that the temperatures of the air and the evaporating surface generally differ, and carelessness in defining saturation deficit. One consequence of difficulties in making the necessary experimental measurements has been practical deviation from the requirements of theory.

(ii) Many workers have not realized the limitations of the Dalton and saturation deficit laws. Some workers have recognized them. Indeed, Edney (1957) has written:

> The saturation deficit law in its general form is ... theoretically unsound. Nevertheless it may be an advantage to know that when adequate precautions have been taken, there is no well authenticated body of information conflicting with the assumption that water evaporates from arthropods at a rate proportional to the saturation deficit provided the temperature is constant, and there is some evidence that it does .... It would not, however, be at all safe to assume that the law applies in unknown cases.

(iii) The saturation deficit and Dalton laws are empirical, but may be useful for expressing evaporation when the following conditions

prevail: (a) steady state evaporation into a calm atmosphere is being evaluated, (b) the supply of energy to the evaporating medium is ample to prevent the rate of formation of vapor from being rate determining, (c) the evaporating surface is sufficiently moist that neither liquid moisture movement to the surface from within the medium nor vapor diffusion to the air interface from evaporation sites within the medium is rate limiting, (d) exterior membranes do not control the rate of evaporation, and (e) experiments of different workers are not being compared.

Factors Affecting Evaporation

The number of atmospheric, soil, and plant factors that must be considered in the evaporation process depends upon the complexity of the system that is to be studied. In this review the external or atmospheric factors, the soil factors, and the plant factors will be considered separately whenever possible in order to establish either a quantitative relationship or a conceptual understanding of the relation between evaporation and the individual factors. This is done in spite of the fact that the various factors are not independent of each other in the overall problem, a realization readily discerned from the physical basis of evaporation given by Penman and Schofield (1941):

> In the summer the surface remains moist only for a short time after rain has fallen; the air gradient is then much steeper than in winter. For the rest of the time the surface is drier and there is also a vapor pressure gradient in the soil. Hence (i) there is more rapid evaporation while the surface is wet, (ii) the total amount of evaporation is dependent upon both total rainfall and on its distribution in time, (iii) the later stages of evaporation are more dependent upon soil conditions than on air conditions, and (iv) the total evaporation is much less than from open water.

The interaction of the various factors is also evident from the results of other workers. Mann (1871) concluded that evaporation from a free water surface depends almost wholly on three factors: the area of the water surface, the temperature of the water at its surface, and the vapor pressure of water in the air above the water. Fortier (1907) concluded that the factors having the greatest influence on evaporation from soils are the quantity of water in the top soil, the temperature of the soil, and air movement.

Quantitative expressions of the degree of relationship between

physical factors and transpiration and evapotranspiration have been obtained. Briggs and Shantz (1916) grew 22 different crop plants in tightly covered pots and obtained correlation coefficients between the transpiration of all crops considered as one population and the environmental factors as follows: temperature, 0.64; wet-bulb depression, 0.79; shallow tank evaporation, 0.72; deep tank evaporation, 0.63; and, wind velocity, 0.26. Ashcroft and Taylor (1953) correlated the water removal from soil by four crops, i.e., evapotranspiration, with various weather factors and found the correlation coefficients of the combined data were 0.713, 0.693, 0.659, and 0.628 between water removal and (i) solar radiation, (ii) open pan evaporation, (iii) temperature times solar radiation, and (iv) temperature, respectively. The agreement between the results of Briggs et al. and Ashcroft and Taylor for pan evaporation (0.67 avg. vs. 0.693) and temperature (0.64 vs. 0.628) is striking.

Atmospheric factors

Windspeed.--In principle, windspeed should affect the evaporation rate by affecting both the turbulence of the air and the thickness of the laminar layer. According to Pasquill (1943), Sutton in 1934 made use of Taylor's 1922 work on diffusion by continuous movements and, in obtaining an explicit expression for the momentum interchange coefficient, deduced the variation of wind velocity with height,

$$\frac{\bar{u}}{\bar{u}_1} = (z/z_1)^{(n/2-n)} \qquad (4)$$

wherein $\bar{u}$ and $\bar{u}_1$ are the mean wind velocities at heights z and z_1, respectively and (n/2-n)-- as deduced for a somewhat different case by

von Karman and Prandtl--has a value of about 1/7. The Sutton theory leads to a functional form for evaporation under steady state conditions which Pasquill developed into a computable form and tested against evaporation from the free surfaces of nine organic liquids and water. He expressed the rates of evaporation relative to that of water--a very unwise procedure in view of the "abnormal", associated structure of water in the liquid phase and the occurrence of the molecular weight in the relation--and concluded that "the theory specifies inadequately the variation of rate of evaporation with type of liquid."

When Pasquill's observed values of evaporation rate, as well as those of other workers Pasquill presented, were plotted as a function of wind velocity on log-log paper a linear relation was found in the range 0.5 to 6.0 m sec^{-1}. These data indicate, then, that a hyperbolic relation between the rate of evaporation from free liquid surfaces and wind velocity can be expected.

Several workers (Houdaille, 1892; Livingston, 1906; Harris and Robinson, 1916; Turnage and Shreve, 1939; Kucera, 1954) noted that the increase in rate of evaporation with air movement is very rapid at the low velocities but that at higher velocities evaporation increases proportionally (Houdaille) to negligibly (Harris and Robinson) with further increases in wind velocity. The only data found in the literature for evaporation of soil moisture, that of Harris and Robinson (1916, fig. 6, p. 450), yield a linear plot of wind velocity on log scale versus evaporation on linear scale. The data reviewed are too meager to conclude whether the present relation or that of Pasquill is the more general. A somewhat relevant observation in this respect is that

of Ceaglske and Hougen (1937) who found evaporation to be greater from sand than from water in still air but greater from water under turbulent air conditions. Their finding is not necessarily a unique function of windspeed, however.

Other relationships have been used. Kolasew (1941) considered and Martin (1943) found the evaporation rate to be proportional to the square root of wind velocity. Houdaille (1885) found an empirical equation containing $(V + 5V^{1/2})$, where V is the wind velocity, expressed the rate of evaporation from a Piche atmometer at any wind velocity.

Turnage and Shreve (1939) found that wet-bulb depression yields a very high correlation with evaporation from atmometers, and that the relation between evaporation rate and wet-bulb depression is linear for any given velocity. The graph they present shows that, for a given wet-bulb depression, the evaporation rate increases as windspeed increases. It would also be suspected, however, that for a given set of field conditions the wet-bulb depression would be greater the higher the wind velocity. The combination of these two effects--increasing evaporation with increasing windspeed at a given wet-bulb depression, and greater wet-bulb depression with increasing windspeed, all other factors held constant--could produce a power dependence of evaporation, from a wet surface, on wind velocity.

Several points must be kept in mind in considering reported dependence of evaporation on windspeed. One consideration is that under field conditions air movements are in gusts whereas studies to establish the dependence of evaporation on windspeed must necessarily be made under conditions of steady air flow. Another consideration is that

climatological records of air movement are generally obtained on a daily basis from anemometers which meter the air movements as length (usually miles) per day. This arithmetic accumulation of a desired logarithmic function may be one cause of the very low correlation between wind velocity and evaporation (Kucera, 1954), transpiration (Briggs and Shantz, 1916) or evapotranspiration. Then, too, since air may move an appreciable distance downwind before establishing a uniform profile the dependence of evaporation on windspeed cannot be assumed to be independent of the geometry of the system. The data presented by Pasquill (1943) illustrate this point. Over the same range of wind velocities, the slopes for the various data are fairly uniform, but there is pronounced displacement on the evaporation rate coordinate.

It could logically be suspected that variability in windspeed might effect mass movement of air within the upper portion of the soil profile. Fukuda (1955) studied the problem and concluded, however, that:

> The soil depth to which air can penetrate as a result of wind gustiness is very slight. Even in sandy soil, the particles of which have a mean diameter of 0.5 - 0.25 mm., it penetrates only about 5 mm. below the surface.

In summary, the literature findings indicate that: (i) Changes in windspeed affect both (a) the turbulent transfer of the water vapor away from the evaporating surface and, (b) the temperature of the evaporating surface. (ii) The relation between windspeed and turbulence yields a power dependence of evaporation on windspeed. The relation between windspeed and wet-bulb depression is apparently unreported. (iii) The quantitative dependence of evaporation on windspeed is not

independent of the geometry of the system studied. (iv) Variation in windspeed does not cause appreciable mass movement of water vapor within a porous drying medium. (v) Reported correlations between windspeed and evaporation are characterized by very low correlation coefficients. This situation is aided by rather meaningless measures of windspeed.

In general, a power dependence of evaporation on windspeed is indicated.

Humidity.--A number of expressions of humidity are used: vapor pressure, relative humidity, dew point, vapor pressure deficit, and wet-bulb depression. This large number of humidity parameters prompted Turnage and Shreve (1939) to suggest that researchers report wet- and dry-bulb temperatures; the interested reader could then calculate the particular parameter of interest to him.

Cummings (1929) derived an equation evaluating the rate of change of evaporation from free water surfaces with the dew point vapor pressure of the water surface. Difficulty was experienced due to non-independence of humidity and the other variables, particularly insolation. Observations indicated, however, that the evaporation rate is a weak function of humidity due to "counter-acting changes in water temperature which result from changes in evaporation caused by changes in humidity."

Harris and Robinson (1916) demonstrated a twenty-fold decrease in evaporation in response to humidity manipulation. Schleusener[3] found that the effect of ambient humidity on evaporation depended upon water

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[3]Schleusener, R. A. 1958. Factors affecting evaporation from soils in contact with a water table. Ph. D. Thesis. Colorado State University. Ft. Collins, Colorado.

table depth. For water table depths greater than 12 inches, changing the humidity of the air had a negligible effect on evaporation from soils.

Plant physiologists have given careful consideration to transpiration as a function of the humidity of the air (Curtis, 1936; Gaumann and Jaag, 1936; others as reviewed by Martin, 1943). The results of Gaumann and Jaag are exemplary. They found that the transpiration rate of Quercus robur in darkness with stomata closed bore an approximately linear relation to relative humidity in the range 10 to 90 per cent at temperatures of 20 and 30° C, but at 40° C the range of linearity was from about 50 to 90 per cent. At all three temperatures there was a tendency for the transpiration at low relative humidities to fall below the value expected from the linear relation. These workers coined the term "physiological saturation deficit" defined as the saturation vapor pressure of water at leaf temperature minus the vapor pressure of water in the surrounding atmosphere.

Quantitative expressions of the relationship between humidity and evaporation or evapotranspiration are scarce. Only two such expressions were encountered in the literature. Lowry (1956) found that the area under the humidity trace on the hygro-thermograph chart, when plotted on log-log paper against evapotranspiration (from a large pan of soil containing some live vegetation), yielded a straight line for short periods of observation. Ceaglske and Hougen (1937) dried one inch thick sand samples in air of constant temperature and measured the resulting weight loss and surface temperature. They found that the drying rate divided by the vapor pressure difference between the sand

surface and the air yielded a nearly constant quotient.

Radiation.--In the general climatoligical and hydrological problem of evaporation the radiant energy is that of the sun. The solar constant is very nearly 2.0 cal cm^{-2} min^{-1}. Interference and filtering by the atmosphere cut this amount down by roughly 1/4. Then, too, deviations from normality between incident beam and surface result from surface slope, declination of the earth and latitude, and rotation of the earth (hour of the day). Taking only these considerations and the latent heat of vaporization of water into account one can readily calculate a logical estimate of the potential annual evaporation for any geographical location. Inclusion of a cloudiness factor, as a percentage of the possible sunshine hours, for example, improves the estimate. Continuation of this procedure with inclusion of arbitrary constants produces empirical, engineering-type equations for estimating evapotranspiration. Such equations will not be reviewed.

Since the role of radiation in evaporation theory has already been considered and the present study does not employ radiant energy as the energy source, review of evaporation as a function of radiation has been summarized in the following statement: Evapotranspiration is in phase with radiation flux rather than temperature (van Wijk et al., 1953; van Wijk and De Vries, 1954), transpiration rate increases with intensity of radiation--at least over a certain range and for certain plants--(Martin, 1943), and effect of radiation on evaporation from soil depends upon the content and distribution of moisture in the soil and upon the severity of other evaporation conditions.

Temperature.--For the insolation evaporation case and a dry evaporating medium all the available energy except that which heats the medium

itself goes into heating the air; in the case of a moist medium most of the energy is used in evaporation. Thus temperature and evaporation or evapotranspiration are correlated, but, since evaporation results in evaporative cooling, the correlation is complicated.

For the wet-bulb evaporation case, lowering of the temperature of the evaporating surface can be very striking. Kamei, Mizuno, and Shiomi (see Gilliland, 1938) obtained a linear relation between steady state rate of drying of 3 cm-thick slabs of clay and wet-bulb depressions, which were as large as 16° C in experiments conducted at dry-bulb temperatures of 15, 25, and 35° C. At a dry-bulb temperature of 65° C Ceaglske and Hougen (1937) measured a temperature drop in the sample of 29° C. Martin (1943) reported that in his experiments the evaporative cooling of the plant leaves in response to transpiration generally did not exceed 10° C. These observations are all compatible with psychrometry theory for the wet-bulb evaporation case.

Staley[4], Schleusener[5], and Schleusener and Corey (1959) measured the temperature profiles in soil columns evaporating under controlled conditions but did not utilize this information in their theories.

Most studies of evaporation as a function of temperature are not the limiting evaporation cases as defined in the theory of evaporation section. In fact, the temperature reported is most often that of the room or the container in which the experiments were conducted. Nevertheless, if all other conditions are held constant as the temperature

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[4]Staley, op. cit.

[5]Schleusener, op. cit.

is varied from run to run, the pattern of results is consistent and acceptably reproducible results are obtained. It is in this sense that evaporation has been studied as a function of temperature in a number of the results which follow:

Dines (1870) demonstrated that, for the rates of evaporation observed, the amount of water evaporating from a free water surface in a room at 62° F would amount to 26 inches per year as compared with 131 inches per year in a room at 88° F. Sleight (1917) observed the evaporation from a series of tanks set outdoors and heated to water surface temperatures up to 16.6° F above the temperature of the control tank by insertion of various numbers of electric light bulbs through the bases of the tanks. His results indicate an exponential increase in evaporation with linear increase in temperature. Any mean weekly surface temperature which exceeded that of the control tank by more than 15° F resulted in at least a doubling of the evaporation rate.

Harris and Robinson (1916) floated shallow aluminum cans containing 25 gm samples of Millville loam and a coarse sand on the surface of a water bath maintained at temperatures of 20 to 90° C. They reported the times, in minutes, required for the soils to reach drynesses of 1/2 the initial moisture percentage and the "practically dry" condition. The temperatures and the corresponding times required for Millville loam to dry to 1/2 the initial moisture percentage, respectively, were: 20°--265; 30°--89; 40°--46; 50°--23; 60°--17; 70°--12.5; 80°--9.5; and, 90°--7. The data show that the average rate of evaporation was 38 times as fast at 90° C as it was at 20° C.

Sherwood and Comings (1933) studied the steady state drying of

fireclay brick batch in circulating air of temperatures 27.8, 43.3, and 65.6° C. The steady state rate of drying was almost four times faster at 65.6 than at 27.8° C. Bateman et al. (1939) calculated the dependence of the diffusion coefficient D on drying temperature for the tangential drying of water-saturated Sitka spruce at temperatures of 35, 40, 50, 60, and 80° C. The relative humidity was 50 per cent at each temperature. The diffusion coefficients were obtained from the expression

$$D = \frac{Q}{At} (L/m_1 - m_2) \qquad (5)$$

wherein Q is the weight loss at time t, L is the length of the wood cylinders studied, and m_1 and m_2 are the moisture contents in excess of the fiber saturation point at the two ends of the cylinders.

Martin (1943) reported studies of evaporation into calm air from leaf-shaped blotting paper evaporimeters and of transpiration by Ambrosia trifida and Helianthus annuus into calm air in darkness with open stomata. Martin's data on evaporation from the evaporimeters show that, at any given relative humidity, the evaporation rate very nearly doubled on increasing the temperature from 27 and 49° C. At a given temperature, the difference in evaporation rate at relative humidities of 20 and 80 per cent was four-fold. Gaumann and Jaag (1936) reported values of transpiration rate at an air temperature of 40° C about five times as great as those for the same "physiological saturation deficit" at an air temperature of 20° C.

The temperature dependence experiments described above all deal with evaporation, transpiration, and moisture flow as rate processes.

It is to such rate processes and to the dependence of the rate on temperature that the theory of chemical kinetics (Amis, 1949; Frost and Pearson, 1953) can be applied. Application of kinetic theory yields apparent activation energies which can be interpreted in terms of energy barriers that might be associated with the mechanism of reaction on the molecular level.

Kinetic theory is to be employed in this study in analyzing the evaporative drying of soil. Although most of the above mentioned results are amenable to treatment by kinetic theory, none of the above authors calculated activation energies.

Biggar[6] did apply kinetic theory to soil moisture flow. He hypothesized that moisture flow into dry soil is an activated process, the apparent activation energy being associated with free energy barriers resulting from the physical and chemical nature of the soil material. The apparent activation energies were calculated from the temperature dependence of the diffusion coefficient D for the wetting of soil columns (infiltration of water into soil). The explicit assumption was made that D takes the form

$$D = D_o \exp(-E^*/RT) \qquad (6)$$

wherein D_o is the diffusion coefficient in the absence of activated diffusion, E^* is the apparent or Arrhenius energy of activation, R is the universal gas constant, and T is the absolute temperature. The calculated energies of activation ranged from 1 to 3 kcal $mole^{-1}$ water depending upon the size fraction of soil used, the density of packing, and the suction of the entering water (Biggar and Taylor, 1960).

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[6]Biggar, J. W. 1956. On the kinetics of moisture flow in unsaturated soils. Ph. D. Thesis. Utah State University. Logan, Utah.

Soil factors

Compaction and layering.--Under isothermal conditions, compaction of soil increases unsaturated liquid flow but results in a lower rate of vapor flow. Harris and Robinson (1916) found that compacting soil at depths below four inches had little if any effect on evaporation. Kolasew (1941) reported results of studies of evaporation from soil columns 15 cm in diameter and 37.5 cm in length into which moist soil was packed in 2.5 cm-thick sections in various combinations of compact and loose layers. The ratio of the bulk densities of the loose:compact soils was 1:1.3. The columns composed of compact or of predominantly compact layers lost more moisture than did columns all or predominantly loose-packed. Based on the initial statement, one concludes that moisture movement in these experiments was predominantly by liquid phase flow.

Ceaglske and Hougen (1937) demonstrated that when a layer of coarse sand is placed upon a layer of fine sand or vice-versa, the rate of drying is independent of the sand below the top layer. With coarse sand on top the constant rate period was proportional to the thickness of the top layer and most of the water was evaporated from this top layer before the finer sand below began to lose moisture.

Water table depth.--Observations on the influence of the depth of the sample on the yield of moisture (Richards and Weeks, 1953; Gardner, 1959a, fig. 7) and on the redistribution of moisture in soil in response to drying (King, 1899; Veihmeyer, 1927; Blaney et al., 1930; Hilgeman, 1948) indicate that the depth of the water table should be an important factor in water loss from soils by evaporation.

Shaw and Smith (1927) concluded that evaporation from Yolo loam is negligible when the water table is more than 10 feet below the soil surface. Schleusener[6] found that for water table depths less than about 12 inches the ambient variables produced approximately the same effect on evaporation from the soils as on evaporation from a free water surface. The observations of Schleusener are in good qualitative agreement with those of Sleight (1917, tables XIX and XX).

The data of Veihmeyer and Brooks (1954, table 4) of cumulative evaporation versus water table depth yield linear plots on log-log paper for water table depths of 1 to 5 feet inclusive. Evaporation from soil with water tables at 1 foot and 5 feet was 62 per cent and 6.2 per cent of the free water evaporation, respectively.

Several workers have made mathematical analyses of water loss from soils above a water table (Wind, 1955; Philip, 1957a, 1957b; Gardner, 1958; Gardner and Fireman, 1958; Visser, 1959). Wind (1955) applied Darcy's law to a study of the optimum depth of the water table in a heavy clay field soil and concluded that unless the water table was within 40 cm of the root zone the flow of moisture to the roots would be less than 0.3 cm depth of water day^{-1}.

Philip (1957a) has presented a solution of the unsaturated moisture flow equation[7] for the case of vertical, one-dimensional, isothermal flow. The equation, which also assumes a unique relationship between

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[6]Schleusener, op. cit.

[7]See page 71 for a brief development of this equation.

moisture potential ψ and moisture content θ is

$$\frac{\partial \theta}{\partial t} = \nabla (D \nabla \theta) + \partial k/\partial z \qquad (7)$$

where in θ is the volumetric moisture content of soil (cm^3 water/cm^3 soil),

t is time (sec),

D is the soil moisture diffusivity (cm^2 sec^{-1}),

k is the capillary conductivity (cm sec^{-1}); $D = k \partial \psi / \partial \theta$

(Klute, 1952) where ψ is the moisture potential, and

z is the vertical space coordinate.

The first term on the right side of equation (7) is the nonlinear diffusion equation with the diffusion coefficient D a function of moisture content. The second term on the right is the gravitational component; this term disappears in the case of horizontal flow.

For steady state flow, equation (7) becomes

$$q/\rho = -D \, d\theta/dz - k \qquad (8)$$

wherein q is the flux of soil water across unit cross-sectional area normal to the direction of flow (gm cm^{-2} sec^{-1}), and ρ is the density of water (gm cm^{-3}).

Philip applied equations (7) and (8) to the transfer of water from a water table at $z = z_w$ (z_w is negative) to a soil surface at which the relative humidity h is specifically h_o. He calculated the steady state flux of water to the surface E (that is, the evaporation rate) as a function of the depth to the water table z_w and the humidity at the soil surface h_o. For this purpose rearrangement of equation (8) yields

$$d\theta/dz = -(k + E)/D \qquad (9)$$

or in integral form

$$z_w = \int_{\theta_s}^{\theta_o} \frac{D}{k - E} \, d\theta \qquad (10)$$

Subject to the assumption that θ is a unique function of the vapor pressure of the surface soil moisture, that is, of h_o, and the conditions that at

$$z = z_w, \quad \psi = 0, \quad \theta = \theta_s$$

where θ_s is the saturation moisture content, relationships of the form

$$z_w = z_w(E, \theta_o) = z_w(E, h_o)$$

or

$$E = E(z_w, h_o) \tag{11}$$

can be found by numerical integration.

Philip considered the dependence of E on h_o and concluded that the flux of moisture E "is virtually independent of h_o, except for a very small part of the h_o range, which we might arbitrarily specify as $h_o > .99$." The basis of Philip's conclusion is the observed small value of the moisture diffusivity D for $h_o \lesssim .99$ (soil moisture suction of 13 bars). Thus Philip considers that since the evaporation rate is independent of h_o for values of $h_o \leq .99$, the moisture flux is a function of water table depth only. Expressed mathematically, relation (11) takes the revised form,

$$h_o \leq .99, \quad E = E(z_w). \tag{12}$$

In his Figure 6, Philip plots E as a function of depth to the water table z_w and summarizes his results in stating:

> ... the evaporation rate from a water-table is either the evaporation rate from saturated soil subjected to the same conditions or a function only of the water-table depth (and the soil characteristics), whichever is the lesser.

Gardner (1958) predicted a maximum evaporation rate limited by capillary conductivity of the soil and the depth to the water table

based on the solution of the moisture flow equation. For the case of soils for which the capillary conductivity k and the soil moisture suction τ, in bars, are related by

$$k = a/(\tau^{n}-b) \tag{13}$$

the maximum rate of evaporation due to movement of the water in the liquid phase, assuming steady state flow and isothermal conditions, is as follows for the various values of n shown:

$$\begin{aligned} n &= 3/2 & E_{lim.} &= 3.77\ ad^{-3/2} \\ n &= 2 & &= 2.46\ ad^{-2} \\ n &= 3 & &= 1.76\ ad^{-3} \\ n &= 4 & &= 1.52\ ad^{-4}. \end{aligned} \tag{14}$$

E is the steady state rate of evaporation (cm day^{-1}), d is the depth of the water table below the soil surface (cm), and a and b are constants obtained, usually, from pressure membrane outflow data (Gardner, 1956). For the relation between k and τ of the form

$$k = a/(\exp - c\,\tau) \tag{15}$$

the limiting rate of evaporation is given by

$$E_{lim} = \frac{a}{\exp(cd)-1} \tag{16}$$

Thus the limiting rate of evaporation is predicted to be inversely proportional to the depth to the water table raised to the same power of n as in the analytical expression relating the capillary conductivity and the soil moisture suction for expressions of the form of equation (13) and inversely to the logarithm of the depth to the water table for relations between k and τ of the form expressed by equation (16).

Visser (1959) considered the solution of the equation

$$dz = \frac{D\, d\psi}{(v\ \psi^n)} \pm 1 \qquad (16a)$$

wherein z is the depth of the water table, ψ is the moisture potential, v is the velocity of capillary flow, D is a constant approximately equal to the permeability of saturated soil, and n varies from soil to soil between about 1.5 and 3.0. In equation (16a) the plus sign is used for upward flow, the minus sign for downward flow, and the capillary conductivity k is expressed by $k = a\ \psi^n$.

Visser developed a nomograph based on the steady state solution of equation (16a) from which the relationship between height above the ground-water table and the soil moisture suction (pF) can be estimated. Equation (16a) includes the relation between capillary conductivity and soil moisture suction like that of equation (13) from Gardner, and a formal similarity with equation (10) from Philip.

Gardner and Fireman (1958) compared the experimental results of evaporation from columns of Chino clay and Pachappa sandy loam, in which water tables were maintained at various depths, with the predictions of equations (14) and found reasonable agreement. Gardner and Fireman concluded that except for shallow water table depths or humid conditions the evaporation rate can be expected to be most frequently limited by the water transmitting properties of the soil. These authors generalized their experimental findings on the two soils studied as indicating that lowering the water table from the surface to a depth less than 60 to 90 cm would be of little use in most soils, since evaporation for this range of water table depths is limited largely by the external conditions.

The data of both Philip (1957a, fig. 6) and Gardner and Fireman (1958, figs. 5 and 6), in agreement with that of Veihmeyer and Brooks (1954, table 4), yield linear plots of water table depth versus evaporation rate on log-log paper. The only exception is the Chino clay soil of Gardner and Fireman for which both the theoretical and experimental plots exhibit a dog-leg, i.e., actually two straight line segments.

In summary, it appears that the steady state rate of evaporation from water tables can be predicted from the moisture flow equation and knowledge of the moisture characteristics of soil. The agreement between prediction and experiment suggests that unsaturated liquid phase flow limits the rate of evaporation. Evaporation rate versus water table depth often yields a linear plot on log-log scales. This is particularly true for water tables of the order of 2 feet or more below the soil surface.

Soil mulches and crop residues.--Utilization of soil mulches has long been recognized as a potential method of suppression of moisture loss by evaporation (Wollny, 1880; King and Jeffrey, 1898; Fortier, 1908; Fortier and Beckett, 1912). A "perfect" mulch is any medium which transports water only in the vapor phase (Gardner, 1958; Hanks and Woodruff, 1958). Most materials, however, unless separated from the soil by an air gap conduct some moisture as liquid flow and are, therefore, "imperfect" mulches.

Livingston (1906) concluded that in desert areas the "evaporating power" of the air is so excessively high that movement of the soil water cannot keep the upper layers moist, and a dry mulch forms which

tends to prevent further evaporation.

Buckingham (1907) studied the effectiveness of dry soil mulches of varying depths and compactness. The mulches were made "perfect" by suspending them above free water or moist soil surfaces in such a way as to provide an air-gap between the mulches and the evaporating surface. In this way water supply to the mulch by liquid flow was eliminated.

Buckingham conducted four separate experiments which appear to constitute the most thorough study of the problem ever made. In his first experiment he studied the influence on evaporation of the moisture percentage of the drying soil. Layers of sandy loam soil, wetted to different moisture contents in the range 10 to 27 per cent, were placed in the bottom of tumblers and the upper 2 inches of the tumblers were filled with coarse sand supported on wire gauze and cheese cloth. An air gap approximately 1/2 inch across separated the mulch from the drying soil. Within experimental error, the loss of water was the same from all soils, indicating that the rate of transfer of the moisture through the mulch limited the process.

The second and third experiments of Buckingham are not directly pertinent to this study, so are not reviewed.

In his fourth experiment Buckingham studied the effect of the thickness of the mulch on water loss. Columns of dry Leonardtown loam and Podunk fine sandy loam 1, 2, 4, and 6 inches in length and of uniform density were placed over containers of water. The experi-

ment ran 140 days. His results were:

Soil	Depth of soil (inches)	Loss of water from the free water surface (inches per year)
Leonardtown loam	1	2.71
	2	1.60
	4	0.95
	6	0.69
Podunk fine sandy loam	1	2.52
	2	1.59
	4	0.93
	6	0.67

In comparison with data presented earlier for evaporation as a function of water table depth these data show the considerable reduction in moisture loss wrought by "perfect" mulches. The difference between soils is not significant.

Buckingham's technique of keeping the mulch from contact with the evaporating medium has been employed subsequently by Harris and Robinson (1916), by Hanks (1958), and by Hanks and Woodruff (1958). Hanks and Woodruff found a soil mulch to be 3 to 5 times as effective as straw or gravel in reducing evaporation. Harris and Robinson concluded that "a thin mulch, if kept dry, is effective in reducing evaporation."

Evaporation suppression by imperfect mulches, that is by mulches in contact with the drying soil, engulf practical field practices and these have been studied. Russel (1939) studied the effect of surface cover on soil moisture losses by evaporation from soil cores 5 inches in diameter and 6 or 7 inches long set out of doors. His overall conclusion was that evaporation losses are decreased by straw mulches mainly during the time when the soil surface beneath them is moist. He attributed residue covers with shading the soil, insulating the soil

from heat conduction and with forming a "dead air" layer across which moisture transfer is by molecular diffusion.

Woodruff (1941) studied the evaporation of water from saturated soils, contained in small jelly glasses, under room conditions of relative humidity and temperature. He concluded that the rate of evaporation is related inversely to the square of the thickness of the dry layer of soil at the surface through which the vapor diffuses.

Gardner and Fireman (1958) whose work on evaporation as a function of water table depth has already been cited, also considered the effect of a surface mulch on the rate of evaporation from soil columns. In a preceding paper (Gardner, 1958) it had been predicted that the evaporation from a soil with a surface mulch should be inversely proportional to the thickness of the mulch, assuming that the rate of movement through the mulch is less than the potential evaporation. To test this prediction, a mulch of 1 to 2 mm diameter screened sand was placed on the surface of a column of Pachappa fine sandy loam with the water table 100 cm below the soil surface. To a good approximation, their prediction was upheld. Their plot of evaporation rate versus depth of the mulch has the same shape as their relation between the depth to the water table and the evaporation rate--as it should have since the predicted relations are both inverse functions of a depth of soil, depth of mulch in one case and depth of soil above the water table in the other. However, the depth scale of the mulch is only about 1/100 of that of the water table depth scale, when both are in the same units. This emphasizes the fact that a small increase in depth of a surface mulch has as much influence on the evaporation rate as does a large

drop in water table depth.

Lemon (1956) calculated the moisture flux by isothermal vapor diffusion as a function of diffusion path length for diffusion of water vapor through air and through sand of 37 per cent porosity. The calculations were for a temperature of 20° C and a vapor concentration difference corresponding to a relative humidity difference of 100 per cent diffusing to 50 per cent.

Hanks (1958) employed Buckingham's technique in studying the influence of depth and porosity on water vapor transfer. He used the equation

$$q = - a \Phi \frac{DM}{RT} \frac{P}{P-p_v} \frac{dp_v}{dx} \qquad (17)$$

of Rollins[8] and Rollins et al. (1954) wherein

q is the vapor flow rate (gm cm^{-2} sec^{-1}),

D is the diffusion coefficient of water vapor into air (0.239 cm^2 sec^{-1} at 8° C),

P is the total atmospheric pressure (dynes cm^{-2}),

p_v is the partial pressure of water vapor (dynes cm^{-2}),

R is the gas constant (8.314 x 10^7 ergs $°Kelvin^{-1}$ $mole^{-1}$),

T is absolute temperature,

M is the molecular weight of water vapor (gm),

x is the distance across the dry layer (cm),

a is a dimensionless tortuosity factor (=.66, Penman (1940)),

and Φ is the volume fraction of air-filled voids.

He found that the ratio of (measured/calculated) flow rate was generally

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[8]Rollins, R. L. 1954. Movement of soil moisture under a thermal gradient. Ph. D. Thesis. Iowa State University. Ames, Iowa.

greater than unity and that the ratio increased as the texture of the soil became finer. The ratio was approximately constant independent of the depth of the dry layer, however.

The data of Buckingham (1907, tables II and III), Lemon (1956, fig. 2-b), Gardner and Fireman (1958, fig. 7), and Hanks (1958, table 2) all have several things in common. They were obtained under isothermal conditions, represent steady state flow conditions, exhibit a common inverse dependence on diffusion path length as required by simple diffusion theory, or, stated another way, all yield linear plots on log-log paper, that is, are hyperbolic on linear coordinates.

The implications of the characteristics of these data merit amplification. The fact that the evaporation rate exhibits the same functional dependence on the depth of mulch as it does on depth to the water table seems to suggest the possibility of similarity in the rate controlling mechanism of flow. When the water table is deep and the soil profile is quite dry, the rate of evaporation is very low. Provided vapor flow is rate limiting, the similarity in mulch and water table depth effects indicates that the rate of evaporation from a soil above a water table must be controlled largely by the rate of vapor diffusion from the evaporation sites within the soil profile.

On the other hand, the observed much weaker dependence of moisture flux on water table depth than on depth of mulch tends to indicate that at constant temperature and under ordinary drying conditions (moisture condition and period of drying of interest in crop production), the contribution of vapor flow to the total moisture flow must be much less than the contribution of liquid flow. For this latter case con-

sistency with observed results of studies with mulches requires that the site of evaporation be very close to the soil surface if not actually at the surface. It is evident that the results depend considerably on the moisture distribution in the drying soil. This facet of the problem will be considered shortly. At present we choose to pursue the observed mathematical relation further, but we must first develop some concepts.

The term "simple diffusion theory" implies that the vapor flux is proportional to the vapor pressure gradient.[9] The general equation expressed mathematically is

$$F = K \frac{\Delta p_v}{L}$$

where F is the flux, Δp_v is the vapor pressure difference across the diffusion path length L, and K is the proportionality constant which includes the diffusion coefficient. If experimental conditions (including temperature) are constant, a steady state flow results. Now, since all the above results are for steady state flow, K and Δp_v can be combined into, say, K'. Hence

$$F\ L = K'.$$

The analytical expression for a hyperbola is

$$x\ y = c$$

where x and y are variables and c is a constant. Graphically, the trace of a hyperbola in any quadrant approaches the x- and y-coordinates asymptotically. This means, in terms of vapor diffusion, that in the limiting case as the diffusion path length approaches zero, the

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[9]For isothermal diffusion as considered here, vapor pressure is proportional to molecular concentration.

vapor flux approaches infinity. But this is contrary to experience; the rate of evaporation, even from boiling water, does not approach infinity, evidently because the available energy input to the system becomes limiting.

Having recognized that vapor diffusion cannot be rate controlling as $L \to 0$, it remains to consider the range of validity of the simple diffusion theory in terms of mulch thickness. Gardner and Fireman (1958) found that when the mulch was less than 3 mm thick, the mulch had no effect on the rate of evaporation. They, therefore, present evaporation data only for mulches ≥ 0.4 cm thick. The thinnest soil layers used by Hanks (1958) were 0.63 cm thick and the experimental results support the vapor diffusion analysis. Lemon's (1956) figure for sand shows that the flux has begun to deviate badly from the predicted straight line on log-log paper for a sand thickness of 0.60 cm (0.25 inches). Evidently a mulch must be of the order of a few millimeters in thickness to cut down evaporation through the entry of vapor diffusion as the limiting process. The necessary mulch depth increases as the soil texture gets coarser.

The data presented earlier on evaporation as a function of water table depth indicate that for sufficiently deep water tables (in which case the surface soil is always dry after a sufficiently long time has elapsed) the observed relation between water table depth and evaporation is consistent in form with simple diffusion theory. The much greater sensitivity of moisture flow to mulch depth than to water table depth suggests that the contribution of liquid flow to the observed flux is appreciable even in evaporative loss of moisture from soils

with water tables as deep as several hundred centimeters below the soil surface.

In summary, both the steady state rate of water vapor diffusion through mulches and the steady state rate of evaporation from soils with a water table exhibit an inverse dependence on flow path length. This is the type of dependence on flow path length predicted by simple vapor diffusion theory. Measurements of the diffusion of water vapor through dry soil mulches are in good agreement with the simple theory provided the mulch is at least a few millimeters in thickness.

Evaporation from water tables exhibits the same functional dependence on water table depth as required by vapor diffusion theory. The reason it should is not obvious. The agreement may be only coincidental since analyses based on the assumption that the evaporation rate is limited by unsaturated liquid flow of moisture also adequately describe this situation. If real, the weak dependence of evaporation rate on water table depth requires that the site of evaporation be close to the soil surface. Whereas it is generally accepted that evaporation occurs at or very near the soil surface when the soil is moist, the weak dependence of evaporation rate on water table depth implies that unsaturated liquid flow occurs to sites of evaporation near the soil surface even in rather dry soil profiles.

Vapor concentration in soil.--Several workers have attempted to measure actual water vapor pressure or relative humidities in the soil. Such studies are necessary since they can yield information directly usable in determining vapor pressure gradients in soils and hence in calculations of the contribution of vapor flow to evaporative

loss of water. The most recent review of the subject is that of John.[10]

Lebedeff (1927) placed a hair hygrometer in boxes of soil at constant temperature and varied the soil moisture content from experiment to experiment. According to John,[11] Lebedeff considered soils under natural conditions to be always saturated with water vapor below a depth of 5 to 10 cm. Fukuda (1956) considered changes in the diffusion of water vapor in relation to its condensation and evaporation in soil pores as determined by measurements ten times daily of flucuations in temperature, relative humidity (an American Instrument Co. electric hygrometer was used), and soil moisture at various depths in soils in the field. Fukuda concluded that at soil moistures yielding relative humidities less than 100 per cent, the observed humidities--not the vapor pressures--are little affected by temperature but depend almost wholly on soil moisture content.

Onchukov[12] (1957) measured the wet- and dry-bulb temperatures of the soil air at 5, 10, 15, 25, 40, and 60 cm. To avoid contact with the soil, the thermocouples were mounted in small metal screen cylinders. The wet-bulb temperature was obtained from thermocouples surrounded by a moistened wadding wick. He concluded that in the surface 5-cm layer there is a sharp lowering of the moisture in the pores.

John[13] conducted experiments with the objectives of (i) finding

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[10]John, P. T. 1958. Vapor pressure gradient and water movement in the top layers of soil. Ph. D. Thesis. University of Washington. Seattle, Washington.

[11]Ibid.

[12]English translation of this Russian article was furnished by Mr. John Cary, Utah State University.

[13]John, op. cit.

out what kind of vapor pressure gradient exists in soil, (ii) determining the effect of wind, temperature, and position of the water table on the vapor pressure distribution, and (iii) correlating the vapor pressure gradient with the evaporation rate and finding out where the evaporation takes place. He waited for steady state evaporation conditions to be established in vertical columns of dry soil supplied with water at their bases, then determined the vapor pressure of air samples extracted with a sealed pump as analyzed by dew-point hygrometry.

In view of his objectives John concluded that: (i) a vapor pressure gradient (a) definitely exists even in moist soil, (b) is strong and linear in the dry soil above the wet front (he wetted vertical columns of soil from the bottom); (ii) wind results in (a) a decrease in the vapor pressure at all levels in coarse sand but only in the top layers of sandy soil, (b) small temperature changes have a greater effect on the evaporation rate than do small differences in water table depth.

In correlating the vapor flux with the vapor pressure gradient, the total moisture transfer was taken as the evaporation rate and the measurement of the vapor pressure gradients enabled the use of the Stefan law type equation of De Vries (1950), which is very similar to that of Rollins[14] (see equation 17, page 33), for calculating the vapor flux. On the assumption that if these two quantities are correct (he considered the maximum error in his vapor flux calculation to be

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[14]Rollins, op. cit.

about 10 per cent for the top layers of soil--dry zone--and about 40 per cent for all other layers) their difference must be attributable to some other mechanism, he took the difference between the total and the vapor transfer and attributed this amount to surface transfer or surface diffusion (Carman, 1956). From this type of approach he concluded that (a) surface flow increases with depth and vapor flow decreases with depth in the soil columns,[15] (b) vapor flow increases relative to surface flow with an increase in temperature, and (c) the smaller the particle size, the greater is the contribution of surface flow to total flow.

In interpreting the results of all these experiments on the measurement of the water vapor concentration in the soil it must be remembered that the methods of measuring the vapor concentration have required a macroscopic sampling interval. This has resulted in obtaining determinations from relatively few locations in a soil profile and in errors in determining the vapor pressure gradient. Consequently, the conclusions of these workers are necessarily similar to those which have been arrived at indirectly by other workers from circumstantial evidence. The fundamental nature of the information to be obtained is worth considerable effort but the first emphasis must be placed on improvements in methodology.

Moisture distribution and site of evaporation.--Evaporation as a function of the moisture distribution seems to have been almost wholly neglected by soil scientists. This situation prompted Staple (1956) to

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[15]Note that this implies evaporation within the soil column.

suggest that "computation of evaporation must be a stepwise process involving the calculation in short time intervals, of both the changing moisture profiles in the drying soil and the resulting evaporation at the surface." The condition has not been much improved even by the advent of elegant solutions of the diffusion equation now available (Crank, 1956; Gardner, 1959) since such solutions are usually presented either in terms of dimensionless parameters or the average moisture content of the whole sample. Difficulty arises in interpreting a dimensionless parameter since it is not always obvious how the components interact to yield the solution; the average moisture content of a soil profile depends considerably upon the depth of soil of interest, a dynamic quantity in practice.

Moisture distribution during drying has been studied by chemical engineers, particularly by Sherwood and co-workers. Sherwood (1932) pointed out that during the constant rate period of drying, the moisture distribution is a parabolic function of the distance from the surface. That is, when moisture content is plotted on the ordinate and distance from the evaporating surface is plotted on the abscissa, a smooth line through the data points has the shape of a parabola about the abscissa. According to Sherwood (1932), Troop and Wheeler (1927), who exposed one surface of clay contained in copper cylinders to controlled drying conditions, were the first to demonstrate this relation. Newman (1931) and Sherwood (1932) have given equations for the relation between moisture content and drying time during the falling rate period for an initial parabolic moisture distribution. Since the same distribution is characteristic of wood drying (Stamm, 1948) the solution of Newman

has been exploited extensively in kiln drying of lumber.

Gilliland and Sherwood (1933) pointed out that the time required to set up the parabolic distribution depends on the nature of the material, its thickness, and the drying rate in the constant rate period. Incorporating these considerations into their analysis they derived an equation expressing the moisture distribution in a drying slab of "brick clay mix" during the constant rate period of drying which enabled them to calculate the length of the constant rate period and the critical moisture content. However, to do so they used the diffusion coefficient obtained from analysis of the falling rate period (Sherwood, 1929a, 1932) and assumed that the constant rate period ends when the surface concentration drops to the equilibrium value. Their function does predict a moisture content which is a parabolic function of the distance from the evaporating surface.

Some workers have attempted to imply the predominant mechanism of moisture flow from a study of the moisture distributions resulting during drying (Hougen et al., 1940; Pearse et al., 1949). Hougen, McCauley, and Marshall (1940) found that capillary flow is typified by a sigmoid-type curve whereas diffusional flow results in a smooth curve concave downward, that is, a parabolic distribution. A survey of the literature indicates very strongly that the parabolic moisture distribution is not completely general; materials as fine as silt if free of a colloidal fraction may not yield the parabolic moisture distribution (Pearse, 1948). It does appear to be characteristic of fine-textured particulate or cellular porous media with appreciable colloidal character. Therefore, it should apply directly to most

soils of agricultural interest.

Closely allied with the moisture distribution is the site of evaporation. The observed accumulation of soluble salts at the surface in arid and irrigated areas is good evidence that when the profile is moist enough for liquid flow to keep pace with evaporative demand, most of the evaporation occurs at the soil surface. Combining the information from the parabolic distribution of the moisture in drying materials with the known dependence of liquid flow on moisture content one can predict that a pattern of moisture distribution will be reached on drying in which unsaturated flow will be unable to keep the surface moist and vaporization at points below the surface must occur if an appreciable rate of evaporation is to be maintained. Sherwood (1929b) states this another way in pointing out that whenever internal liquid diffusion is controlling there is a tendency for the locus of evaporation to retreat into the solid. At any rate, drying of the surface layer ensues and a natural mulch results. Since in the treatment of mulches already given it was shown that at such drynesses, vapor diffusion becomes evaporation rate controlling and vapor diffusion theory is compatible with the observations, only the site of vaporization need be considered here.

The extensive experiments of Buckingham (1907) were prompted, in fact, by a desire to study evaporation from points below the surface. His results show that the deeper in the profile evaporation occurs the lower the evaporation rate must be. Onchukov (1957) used the difference between the wet- and dry-bulb temperatures of the soil air as an indication of the zone of evaporation. On the basis of this criterion

his results predict that no evaporation should occur below 25 cm but that extensive evaporation occurs within 5 cm of the soil surface. Onchukov's measurements indicated that on both heating and cooling the soil particles change temperature faster than does the air in the pores, an observation consistent with evaporation of moisture from the soil particles into the air pores during the day and condensation of moisture on the particles from the warmer air at night.

Richards et al. (1956) followed the moisture distribution for a period of two months in a soil profile thoroughly wetted initially with saline irrigation water. They concluded from moisture distribution and salt accumulation data that under the conditions of their experiment water vapor transfer was agriculturally insignificant below the 15 cm depth.

Sherwood (1930) hypothesized that if evaporation takes place at a plane a definite distance from the surface there should be a discontinuity in the moisture gradient curve at the plane of evaporation. On plotting moisture sampling curves (i.e., moisture percentage versus distance) he found no evidence of a discontinuity, however, and concluded that the data obtained eliminate the possibility that the evaporation occurs at a retreating plane, or even in a narrow zone.

Sherwood (1929b) observed that the site of evaporation apparently depends upon the porosity of the drying medium. He probably should have said pore size instead of [total] porosity, however. Experiments have shown that a dry layer is detectable in sand (Ceaglske and Hougen, 1937; Woodruff, 1941; Pearse, Oliver, and Newitt, 1949) but is difficult to define in finer textured materials (Sherwood, 1930), even

though the finer materials normally possess greater total pore space. Peterson[16] used the electrical conductivity of the saturation extract to study salt accumulation in the profiles of loose, porous high organic soils. He found the 1/2 to 1-inch sampling interval exhibited decidedly higher electrical conductivities than either the 0 to 1/4-inch or the 0 to 1/2-inch sampling interval. The evidence is good that maximal evaporation occurred at a depth 1/2 to 1 inch below the soil surface in these soils.

Plant factors

Of the components of the general evaporation problem the economic interest is usually focused on the plants. It is their parts, products, and byproducts which have value on the market. Therefore, for the sake of completeness, it is necessary to make some statements about their role even though they are absent in the present study. In the main only concepts will be presented.

Land plants have developed certain characteristics which make their survival possible (Bernstein, 1955). One of these features is flattened leaves of large surface area which present maximum surface area for the absorption of light energy and the interchange of gases with the environment. In addition, the interior of the plant leaf is made up of cells loosely arranged with continuous but irregular air spaces between the cells. The air spaces are interconnected and lead to the exterior atmosphere through pores in the leaf surface called stomata. This hollow leaf structure with openings to the atmosphere via the stomata facilitates the exchange of carbon dioxide and oxygen. Both the large surface area of the leaves and the provision for the

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[16]Peterson, H. B. 1959. By personal communication.

ready exchange of gases facilitate photosynthesis.

These adaptations of land plants for maximum photosynthetic advantage have been a detriment to the plants from another point of view. The cell walls inside the leaf must be kept moist, but the moisture from their surfaces evaporates then diffuses out through the stomata into the surrounding air. This evaporative loss of water from plants is called transpiration. Because of the magnitude of this water vapor loss by transpiration (it ranges from 0.5 to 2.5 gm water dm^{-2} leaf hr^{-1} under favorable conditions for water loss to as low as 0.1 gm dm^{-2} hr^{-1} or less for low temperatures, at night, or when soil moisture suction is high--Meyer and Anderson, 1952) plants require extensive, finely divided root systems for absorption of water. Most of the water absorption is through the root hairs which occupy a space of a few millimeters to several centimeters behind the zone of elongation of the root tip. From a physiological point of view Meyer and Anderson view the number of root tips borne by a root system as probably the most important index of its effectiveness in obtaining water.

Also consistent with the magnitude of transpirational losses of water, plants have developed specialized, greatly elongated cells in the roots, the stems, and the leaves which form a continuous system of hollow tubes called xylem. This continuous water conducting system connects the root hair zone of the plant with the mesophyll cells of the leaf. Loss of water by leaf cells results in a reduction of turgor; the cells then absorb water from the conducting vessels with increasing intensity. That, in turn, causes more water to move into the root and along the water-conducting elements from the plant root cells. The

net effect necessitates an increased rate of absorption of water by the root cells in contact with the soil moisture in order to keep the plant cells adequately supplied with water.

With the above concepts in mind the analysis of the plant factors in evapotranspiration, the sum of evaporation plus transpiration, is more meaningful. Van den Honert (1948) pursued Gradmann's idea of 1928 of applying an analog of Ohm's law to the water transport through the plant as a whole. (In theory this is valid for diffusion as well as for flow through capillaries.) For steady state transport through the plant the rate of water transport (dm/dt) in each part is the same. Designating the resistances in the root cells, xylem, leaf cells, and the "gaseous part" by R_r, R_x, R_e, and R_g, respectively, and designating the potentials (biologists use diffusion pressure deficits symbolized by DPD; these are equivalent osmotic pressures) in these same parts by P_1, P_2, P_3, and P_4 he wrote

$$\frac{dm}{dt} = \frac{P_1 - P_0}{R_r} = \frac{P_2 - P_1}{R_x} = \frac{P_3 - P_2}{R_e} = \frac{P_4 - P_3}{R_g}. \qquad (18)$$

P_0 is the DPD of the moisture supply external to the roots.

If reasonable values of the DPD of the air of 1000 atmospheres (relative humidity of 47 per cent at 20° C), of the chlorenchyma cells of 50 atmospheres, and of lesser values for the other components down to zero atmospheres DPD for P_0 (free water or saturated soil) are assumed, and if all the effects between the soil and the air are considered as one unit and those between the plant and the air as another unit, then $(P_4 - P_3)/(P_3 - P_0) \approx 20$. Therefore, $R_g \approx 20\ (R_r + R_x + R_e)$, that is, the effective resistance in the gaseous part is about 20 times the sum of the resistances offered by the other parts. Van den Honert

considered the great resistance in the gaseous part of the system to be a physical reality. He states:

> In our case, the conclusion is inevitable that the master-process is always, under any circumstance, the transport in the gaseous part. Generally it will be a diffusion process. However, under special circumstances (amphistomatous leaves, small radiation, open stomata) heat conduction through the same air layer may partly take over the role of master-process.

Philip (1957b) made a directly analogous analysis in terms of the specific free energy of each segment of the soil-plant-atmosphere continuum and reached the same conclusion as did van den Honert.

The effectiveness of the stomata in control of transpiration is much debated. Penman and Schofield (1951) considered that all the separate diffusion streams passing out through the stomata merge at a short distance from the leaf surface, and that thereafter the bulk flow encounters resistance as it moves away from the leaf. These workers considered the external resistance to overwhelm other considerations to such an extent that under still conditions, stomatal control of transpiration is very slight and the stomata must be nearly closed before they cut down the rate appreciably. As air motion around the leaves increases, the external resistance decreases and the stomatal movement becomes a more significant factor. Essentially, this viewpoint amounts to assuming that the stomatal component of resistance is about the same independent of external conditions.

The analyses mentioned above point to the conclusion that transpiration is, in the main, a physical process and should therefore be readily amenable to the application of physical principles. It is almost incomprehensible, however, that plants should not exhibit some physiological control over transpiration. That they may is supported by the facts

that the stomata occur at the point at which protection against the physical system is most critical and at the only point at which protection would be effective, namely at the plant-air interface.

Phenomena of Drying

Stages of drying

It is commonly accepted that there are three stages or periods in the drying of porous solids with moisture loss by evaporation. These stages are a constant rate period and two falling rate periods (Fisher, 1923; Sherwood, 1930; Sherwood and Comings, 1933; Kolasew, 1941; Pearse et al., 1949; Marshall, 1950; Lemon, 1956). These stages of drying are usually identified by plotting the evaporation rate, as determined by weighings at arbitrary time intervals, against the average moisture content of the sample. There are other procedures, however (Marshall, 1950).

During the constant rate period of drying moisture flow to the evaporating surface is rapid enough that the rate of evaporation is limited by external conditions. Empirical relations found to hold for evaporation from free water surfaces may be applied. The moisture content at which the constant rate period ends and the falling rate period begins is termed the critical moisture content. In general, the higher the evaporation rate during the constant rate period the higher is the critical moisture content (Buckingham, 1907; Penman, 1941). Under laboratory conditions of evaporation Penman (1941) found the rapid initial drying of soil columns radiated by a 750-watt lamp suspended 2 feet above the soil surface lasted about two days.

Sherwood and Comings (1933) presented data on the drying of several clays, sands, and ceramic plate and from the effect of air temperature, humidity, and air motion on the rate-of-drying curves concluded that the two distinct falling rate periods of drying are

characterized by a mechanism of drying which changes abruptly from surface evaporation controlling in the first falling rate period to internal liquid diffusion controlling in the second falling rate period of drying. Several workers (Keen et al., 1926; Ceaglske and Hougen, 1937; Pearse, 1948; Pearse et al., 1949; Marshall, 1950) considered the first falling rate period to begin when a sufficient number of surface sites (individual soil particles, for example) become dry to decrease the surface area from which evaporation occurs. Others (Penman, 1941; Lemon, 1956; Gardner, 1959) consider the falling rate period to begin when the entire soil surface reaches a moisture content in equilibrium with the air. Of these interpretations, the first seems the more likely and realistic. Published actual drying rate curves show the various periods grading smoothly into each other. This behavior would be expected if the former case held. In reviewing the literature the impression is obtained that the majority of researchers consider evaporation to occur predominantly from the soil surface during the first falling rate period. In this case the rate should be sensitive to evaporation conditions.

When the second falling rate period begins the surface is dry and evaporation takes place within the solid, the vapor reaching the surface by molecular diffusion. There may still be liquid phase movement in the zone of evaporation but it is very slow. The evaporation rate during this period is not readily susceptible to environmental changes (Sherwood, 1929b; Hougen et al., 1940) but the rate is a function of sample thickness--inversely proportional to it (Sherwood, 1929b). Sherwood (1930) considered that the actual evaporation takes place at such a distance from the surface that the rate of diffusion of vapor

through the solid and through the laminar air film is equal to the rate of internal liquid diffusion.

Sherwood (1929b) gives descriptions of the various cases of drying, which correspond closely to the constant and first and second falling rate periods in that order as follows:

> I. Evaporation of the liquid at the solid surface; resistance to internal diffusion of liquid small as compared with the resistance to removal of vapor from the surface.[17]
>
> II. Evaporation at the solid surface; resistance to internal diffusion of liquid great as compared with the resistance to removal of vapor from the surface.
>
> III. Evaporation in the interior of the solid; resistance to internal diffusion of the liquid great as compared with the total resistance to removal of vapor.

Sherwood's second case is the only one which is difficult to visualize. It seems to be self contradictory.

Mechanisms of flow of moisture

Considerable effort has been put into trying to explain the drying rates and the moisture distributions in terms of various mechanisms of flow. Pearse et al. (1949) state:

> The forms of the drying rate curves vary with structure and composition of the solid, but exhibit common characteristics which may be related to the mechanism by which moisture is being removed from the system at any moment.

Of particular interest with respect to this statement is the work of Keen (1914), who suspended two soils, sand, and silt over sulphuric acid solution. He found the plots of moisture percentage versus time for sand and silt to be linear over a wide moisture content range;

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[17] See pages 54-55 for a clarification of Sherwood's interpretation of the term "diffusion."

similar plots for soil exhibited a slight but definite curvature. Igniting the soil to dull red heat changed the type of evaporation curve to one "identical" with the sand curves. After having studied the evaporation from china clay and the lack of effect of removal of humus by 2 per cent NaOH solution, Keen concluded that the colloidal nature of clay is mainly responsible for the characteristic shape of the evaporation curve of soil.

In discussing the physical nature of the soil complex Fisher (1923) pointed out that for the most part typical colloidal materials such as wool, cotton, and gelatin when in equilibrium with a given moisture content have the water uniformly distributed throughout the mass. He described soil as "a collection of relatively non-hygroscopic non-colloidal particles of irregular and variable shapes and sizes with a gelatinous or colloidal coating." Fisher went so far as to propose that the moisture content of soil be calculated not as a percentage of the total weight of dry soil but on the basis of the weight of the dry soil colloid. In practice the idea meets with difficulty; it has never been adopted.

Hougen et al. (1940) and Pearse et al. (1949) have listed the driving forces by which water may be moved or distributed (or which cause resistance to movement) during drying, but Marshall (1950) presents a more complete listing. Marshall's list of the internal mechanisms of liquid flow includes: (i) diffusion in continuous, homogeneous solids, (ii) capillary flow in granular and porous solids, (iii) flow caused by shrinkage and pressure gradients, (iv) flow caused by gravity, (v) flow by a vaporization-condensation sequence, (vi) flow

by an electrical potential (electroosmosis), and (vii) flow caused by temperature gradients (thermal diffusion).

Before considering different workers' interpretations of their results in terms of the various mechanisms of flow it is necessary to clarify the two contrasting philosophies that have arisen in the use of the term "diffusion." One school of thought--that of the workers Ceaglske, Hougen, Marshall, McCauley, Newitt, Oliver, Pearse, and those with whom they co-author--considers diffusion in the classical sense as the distribution of the molecules within a single phase brought about by molecular motion of translation and mutual bombardment. Strict adherence to this definition results in this group of workers having to interpret practically all experimental results, save those for the second falling rate period in which vapor diffusion predominates, in terms of capillary phenomena.

The other school of thought adheres to no strict definition of diffusion but uses mathematics as its criterion of categorization. If the mathematics of diffusion can be applied and is found to express the observations satisfactorily, the gross phenomenon is considered one of diffusion. This group has been led by Sherwood and his co-workers, mathematicians (Jost, 1952 and Crank, 1956, for example), and those associated with the lumber industry--in general, by those who have actively used diffusion equations. Soils workers who have solved the unsaturated flow equation have developed an awareness of the need for clarification, and since about 1950 a convention has been growing, the essence of which is as follows: Due to the formal similarity between the equations of heat flow, diffusion and unsaturated moisture

flow, refer to the moisture flow equation as a "diffusion type" equation and to the quantity in the flow equation analogous to thermal diffusivity in heat flow as the "soil moisture diffusivity."

Individuals of this latter school of thought, including the soils workers, have not concerned themselves very much with a physical interpretation of the mechanism of flow nor with the definition of diffusion. The mathematics is the same whether diffusion equations or diffusion type equations are used.

The situation is not good and indications are that it will get worse. Some of the reasons are: (a) The classical definition is too restrictive to be of much value in describing flow in multiphase systems. (b) In contrast with (a) above, the mathematics of diffusion does describe the flow of water and other liquids through porous media. (c) The ever increasing number of methods of solving the differential equation of diffusion, with the concentration dependence of the diffusion coefficient taking almost any form, promises to extend the application of mathematics of diffusion solutions to problems heretofore too complex for accurate mathematical expression.

The situation focuses attention on the need for a critical evaluation of terminology and/or development of new analytical approaches.

Marshall (1950) pointed out that the drying process cannot be considered apart from the complex structure of the substance to be dried and that gravity, capillarity, and vaporization-condensation are equally as important as diffusion. Hougen (1940) stated that the term diffusion should be restricted to the molecular movement of vapors where convection is negligible and to the motion of water molecules in

homogeneous solids.

In view of the above statements and the complexity of solid-liquid-gaseous phase interactions in porous media let it suffice to present a cross-section of concise statements concerning flow mechanisms. Barrer (1948) and Carman (1948) give the following respective statements on the flow of water in porous materials.

> There are various ways in which a fluid such as water may be transported in a porous medium. The transport mechanisms depend upon pressure, physical state of the fluid (gas or liquid), the nature of the capillaries (their diameter, length, shape, roughness and regularity), the temperature, the isothermal or adiabatic condition of flow, and sometimes upon surface tension.
>
> The permeability of a medium to water or any other fluid under the action of a pressure difference may arise in various ways.
>
> (i) The fluid may dissolve and be transported by diffusion along a concentration gradient produced by the pressure difference.
>
> (ii) In a porous medium, the fluid may be absorbed at the interwall of the capillary structure and be transported by diffusion along a concentration gradient.
>
> (iii) The fluid may flow through capillaries of a porous medium at a rate limited merely by its viscosity.
>
> No sharp line separates these processes and it is possible for all to be involved simultaneously.

Barrer (1951) considered that the nature of the movement of water, organic vapors, or gases depends primarily upon the manner in which the diffusing substance is held inside the solid, and on the nature of the channels. He considers that the sorption may be: Van der Waal's sorption, dipole sorption in a monolayer, multilayer sorption at higher humidities with possible orientation, and capillary condensation in pores. The sorption forces mentioned by Barrer are believed to be operative and appreciable in the moisture range of availability to plants (Babcock and Overstreet, 1957; Passerini, 1954; Taylor and

Stewart, 1960).

When the interpretation of drying is made in terms of capillary phenomena the explanation is similar to the one given by Comings and Sherwood (1934):

> The water rises to the surface through any system of interconnecting passages until all the various menisci at the lower ends of the water columns have the same radius of curvature as the small menisci at the surface from which evaporation is taking place. As the drying proceeds, a time will be reached when the menisci at the lower ends of the water column in any system of interconnecting passages are, in general, about the same size as the smallest cross-section of the surface openings, and water will no longer be drawn to the surface through these passages. Evaporation will continue from the surface menisci, and the water in these surface openings will be depleted, thus causing the retreat of the surface menisci into the solid.

Van Vorst[18] described the drying process in response to passing air over the upper end of soil columns in a vertical position as follows:

> As air, or other carrier gas, flows over the drying surface, liquid will be evaporated from the surface, and the surface layer will therefore tend to desaturate. This will cause an increase in the capillary pressure (the difference in the gas and liquid phase pressures), and therefore a decrease in the pressure in the liquid phase. Flow will then take place in the liquid phase, in the direction of decreasing pressure. In this manner, the lower regions furnish liquid water to the drying surface, and all evaporation takes place at the surface. This mechanism can continue until the liquid distribution has reached a value such that flow by capillary forces can no longer be supported....Subsequent drying must be by vaporization "in situ" and diffusion into the drying atmosphere. These two general drying procedures will be referred to as the "capillary period", and the "diffusion period."

Apparently on the basis of experimental evidence that if the cells of wood are not fully saturated each cell will contain an air bubble,

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[18]Van Vorst, W. D. 1953. The internal mechanism of the drying of granular materials. Ph. D. Thesis. University of California. Los Angeles, California.

Stamm (1948) described the general mechanism of liquid flow through wood as follows:

> In a series combination of fibre cavities containing equal-size bubbles, the flow of liquid toward the wet line will occur first from the fibre cavity nearest the surface because the distance of flow and hence the resistance to it, will there be least. The bubble within the fibre cavity will expand, as flow takes place, until it practically fills the cavity. The bubble meniscus will then tend to be pulled into one of the pit orifices. This pull will increase the curvature of the bubble to a point at which the resistance to further expansion exceeds the resistance to expansion of the air bubble in the next fibre cavity. Flow will then occur from this second fibre cavity until its bubble practically fills the cavity....The water in the second fibre cavity from the wet line can therefore pass through channels between the bubble and the fibre wall of the first cavity from the wet line. This will increase the resistance to liquid flow, but will not prevent it.

This description of the process is of more than academic interest to soils workers since it focuses attention on a facet of the drying process which has been almost completely ignored heretofore by this group, that is, details of the mechanism by which air flow into the porous medium proceeds as the air-filled porosity of the sample increases due to desaturation. The effects might be significant, at least in fine textured soils.

Hougen et al. (1940) who are proponents of the classical definition of diffusion gave the following general summary of the mechanisms of moisture transfer.

> In the drying of solids movement of liquid water by diffusion is restricted to the equilibrium moisture content below the point of atmospheric saturation and to single phase solid systems in which the water and solid are mutually soluble. The first category applies to the last stages in the drying of clays, starches, flour, textiles, paper and wood, and the second category to the drying of soaps, glues, gelatins, and pastes.

> Water held in interstices of solids, as liquid covering the surface, and as free water in cell cavities is subject to movement by gravity and capillarity provided passageways for continuity of flow are present. Water flow in drying due to capillarity applies to water not held in solution and to all water above the fiber saturation point, as in textiles, paper, leather, and to all water above the equilibrium moisture content at atmospheric saturation, as in fine powders and granular solids, such as paint pigments, minerals, clays, soil and sand.

In summary, it appears that due to the complexity of the soil system, the multitude of interacting forces, and confusion in terminology it will be quite impossible to give unequivocal interpretation to the mechanisms of moisture flow in soils. Attempts to do so should not be condemned, however, because considerable clarification in thought can result from carrying a given analysis to a logical conclusion, and limiting cases can be well defined. Simpler systems may profitably be studied but extrapolation of the results to the soil system must be made with caution.

Analyses of Drying

Evaporation as a function of time

Several workers have studied the drying of soil suspended above sulphuric acid in desiccators. On examining the drying curves of soil, sand, and silt mathematically, Keen (1914) found an exponential relation was required to fit the data for soils whereas a simple linear relation existed between moisture percentage (oven-dry weight basis, θ_w) and time for sand and silt. The equation he developed to apply to soils is

$$A \frac{d\theta_w}{dt} = \sqrt[3]{(\theta_w s/100) + 1} \left[2.303 \log_{10} (\theta_w + K) - \log_e (K)\right] \quad (19)$$

wherein θ_w is the percentage water by weight

s is the specific gravity of the soil,

$d\theta_w/dt$ is the rate of evaporation, and

A and K are constants.

Fisher (1923) believed Keen's equation to be an incomplete expression for the relation between time and moisture content and that the true curve is really of a more complex type. He wrote rate equations for the constant and first and second rate periods, in that order, as follows:

$$-d\theta_w/dt = k_1 \quad (20)$$

$$-d\theta_w/dt = k_2 \theta_w \quad (21)$$

$$-d\theta_w/dt = k_3 (\theta_w - C) \quad (21a)$$

wherein k_1, k_2, and k_3 are rate constants and C is the intercept on the abscissa resulting from extrapolation of the initial portion of the second falling rate curve to the horizontal axis. Fisher considered

moisture flow within the sample to be rate limiting. Veihmeyer and Hendrickson (1955) presented graphically their results for evaporation of water from thin layers of soil. Their graphs of moisture content versus time are hyperbolic, the sharp change in the rate occurring at approximately the permanent wilting percentage.

Penman (1941) mentioned that his results for evaporation from soil columns approximately fit the relation $E = at^{1/n}$ wherein E is the total evaporation after t days, a is a constant, and n equals approximately three. Richards et al. (1956) studied the moisture changes in 2.63 meters square field plots of Pachappa sandy loam by gravimetric sampling. They found that for surface layers of soil of thickness 10 to 50 cm the amount of water remaining in the soil θ_r, in surface inches, could be expressed by

$$\theta_r = at^{-b} \tag{22}$$

in which t is time in days and a and b are constants. In equivalent form

$$\ln \theta_r = \ln a - b \ln t \tag{23}$$

in agreement with which they obtained linear plots of log θ_r against log t. Differentiation of equation (22) yields

$$d\theta_r/dt = -abt^{(-b-1)} = -b\,\frac{\theta_r}{t} \tag{24}$$

which shows that the rate of change of the amount of moisture in the soil is directly proportional to the moisture content θ_r and inversely proportional to time.

The results of a number of different workers who give the yield of water Q from soil for a given flow geometry as a function of time t

can be expressed by

$$Q = a\, t^{b}. \tag{25}$$

The experimental conditions under which the data were obtained are given in Table 1. This general time dependence for moisture flow during desorption has not been previously reported.[19] It is of interest here,

Table 1. Examples from the literature of moisture yield by soil which fit the equation $Q = a\, t^{b}$.

Reference	Flow geometry	Flow induced by (driving force)	Initial moisture condition
Ubell (1956)	Radial, but some well drawdown	Pumping a well	Saturated
Read[d] (1959)	Radial (disc of soil)	Vacuum pump suction on filter cone	Saturated; unsaturated[c]
Vasquez and Taylor (1958)	Small tensiometers normal to axis of large cylinder	Vacuum pump suction on filter cone	Unsaturated[c]
Richards and Weeks (1953)	Linear, horizontal	Vacuum pump suction on a ceramic plate	Unsaturated[c]
Richards et al. (1956)	Linear, vertical	Atmospheric conditions	Field capacity

[c]By the nature of the method used, the soil moisture could at no time exceed the equivalent of about 1.0 bar suction.

[d]Read, D. W. L. 1958. Horizontal movement of moisture in soil. M. S. Thesis. Utah State University. Logan, Utah.

[19]The dependence of water infiltration on $t^{1/2}$ and its expression in the more general $Q = a\, t^{b}$ form is well known and widely recognized. A similar recognition of the time dependence of the drying process has never developed. Crank (1956, pp. 276-280) discusses the time dependence of both absorption and desorption. At a later point in this report (see pp. 74-75) the relation between infiltration and drying is considered more fully and the apparent reason for the lack of recognition of the time dependence of desorption is alluded to.

however, because (a) the proposed study is to deal with the time dependence of the drying of soil columns, i.e., the rate aspect of the process, (b) the relation apparently holds over a wide range of moisture conditions and flow geometries, and (c) the relation is independent of the "driving force" associated with the flow. Considerations (b) and (c) accentuate the fundamental significance of the microscopic flow process per se in contrast with the gross phenomenon expressed in terms of fluxes and driving forces.

In all the studies summarized in Table 1 the moisture flux decreased with time. Evidently the molecular flow processes could not maintain the initial rate of flow. Their failure to do so is manifest in a macroscopic flow coefficient which changes with time and the development of a moisture gradient exhibiting the lowest moisture contents nearest the extracting surface (Richards and Weeks, 1953). This explanation of the cause of transient unsaturated moisture flow illustrates how microscopic flow processes dominate the macroscopic moisture flux.

Moisture flow

Capillary equations.--A number of workers (Comings and Sherwood, 1934; Ceaglske and Hougen, 1937; Oliver and Newitt, 1949; Pearse, Oliver, and Newitt, 1949; Van Vorst[20]; Miller and Miller, 1955) have given attention to capillary effects in drying. The results of these studies considered as a whole indicate that capillary theory (Haines, 1926; Smith, 1932; Carman, 1953) is unable to describe moisture dis-

[20]Van Vorst, op. cit.

tribution and movement except in very coarse, non-colloidal materials. Ceaglske and Hougen (1937) claimed to be able to calculate the water distribution in sand of average radius 0.64 mm for any bed thickness and for any average water content. The scheme devised could not be used for suction greater than 12.5 cm water, however, because at greater suctions the water films started breaking at the top surface and drying of the films occurred in situ producing a layer of equilibrium dryness at the surface.

Pearse, Oliver, and Newitt (1949) developed a theory based upon the assumption that the water moving to the surface is always in the form of continuous "filaments or threads" in the pores of a bed consisting of uniform, spherical, non-porous particles. Beginning with the Poiseuille equation for streamline flow through particulate systems an equation for calculating the head of fluid required to maintain flow (overcome frictional forces) was obtained. During the course of its development the effects of the configuration of packing and curvature of the moisture films (capillary effects) and the depth of the bed (gravitational field) were introduced. The equation arrived at is

$$\frac{P_s - P_d - h}{h} = \frac{3.25 \times 10^{-5} A}{y r^2} \qquad (26)$$

wherein P_s is the suction potential at the surface (cm water),

P_d is the suction potential at the depth h (cm water),

A is the drying rate (gm cm^{-2} hr^{-1}),

y is the percentage of "fine" pores at the surface, and

r is the radius of the spheres (cm).

The constant 3.25×10^{-5} includes the fractional porosity of the bed, the specific surface of the particles, and the density and viscosity

of the water. Based on calculations in which P_g, A, and h were varied systematically Pearse and co-workers predicted that in the particle range 10^{-1} to 10^{-2} cm gravitational and capillary forces are rate controlling; in the particle range 10^{-3} to 10^{-4} cm capillary forces are rate controlling; and in the particle range 10^{-5} to 10^{-6} cm capillary and frictional forces are limiting. These predictions were tested using glass spheres of radius 60 x 10^{-4} cm and silica flour of average radii 23.5 x 10^{-4}, 7.5 x 10^{-4}, and 2.5 x 10^{-5} cm. They concluded that the theory applies apparently satisfactorily for coarse materials but requires modification to be applicable to fine particles--because of vaporization within the bed itself upon development of high suctions, they said.

Miller and Miller (1955) describe their theory of capillary flow based on the assumption that the classical laws of surface tension and viscous flow govern the behavior of liquids within the microscopic pores and channels of unsaturated porous media. The authors enumerate many assumptions of the theory. It, too, is only applicable to the coarse silt and sand particle size range of soils.

Diffusion equations, constant diffusion coefficient.--The general differential equation for variation in moisture content at any point in a unidirectional flow system is given by

$$\frac{\partial \theta}{\partial t} = D \frac{\partial^2 \theta}{\partial x^2} \qquad (27)$$

wherein θ is the moisture content subject to diffusion per unit weight of dry sample (gm gm^{-1})

t is elapsed time (sec)

D is the diffusion constant of the liquid (cm^2 sec^{-1}) and

x is the space coordinate (cm).

Hougen et al. (1940) have summarized the available solutions of equation (27) with D constant subject to the assumptions

(i) the differential equation for diffusion is valid for drying

(ii) the diffusion coefficient is constant

(iii) the diffusion is wholly normal to the surface plane

(iv) shrinkage is negligible

(v) the drying conditions remain constant

for different boundary conditions in the drying of a slab of thickness 2L (infinite case assumed) from both surfaces. For these solutions x is measured from the midplane in the direction of diffusion.

Constant rate of drying.--Case I. At time zero the moisture content is uniform throughout the sample; after the experiment begins the rate of evaporation is constant from each end of the sample, or

$$\text{at } t = 0 \qquad \theta = \theta_o \qquad -L \leq x \leq L$$

$$\text{at } t \geq 0 \qquad \left(\frac{\partial\theta}{\partial x}\right)_{x=L} = a \text{ and } \left(\frac{\partial\theta}{\partial x}\right)_{x=-L} = -a \tag{28}$$

wherein θ_o is the initial uniform moisture content and

a is the constant rate of drying (gm cm^{-2} sec^{-1}).

The solution (Gilliland and Sherwood, 1933) is

$$\frac{(\theta_o - \theta)D}{a\,L} = \frac{(x-L)^2}{2\,L^2} - \frac{1}{6} + \frac{Dt}{L^2} + \frac{2}{\pi^2}\sum_{1}^{\infty}\frac{(-1)^m}{m^2}\,e^{\left(\frac{-D\pi^2 m^2 t}{L^2}\right)}\cos\frac{m\pi(x-L)}{L} \tag{29}$$

The solution predicts that as t becomes large, θ approaches a parabolic function of x. However, the data of the calculated curve of moisture distribution in brick clay mix presented by Gilliland and Sherwood yields a semi-log plot already at 0.5 hr.

Falling rate of drying.--Case II. At time zero the moisture content is uniform throughout the sample but as soon as drying begins the moisture content at the evaporating surface drops to the equilibrium moisture content, or

$$\begin{aligned} &\text{at } t = 0 \quad \theta = \theta_o \qquad -L \leq x \leq L \\ &\quad t > 0 \quad \theta = \theta_e \qquad \text{at } x = +L \text{ and } x = -L \end{aligned} \tag{30}$$

wherein θ_e is the moisture content of the sample in equilibrium with the drying conditions.

The variation in moisture content at any point with time is given (Sherwood, 1929a; hougen et al., 1940) by

$$\frac{\theta - \theta_e}{\theta_o - \theta_e} = \frac{4}{\pi}\left[\cos\frac{\pi x}{2L}\, e^{-Dt\left(\frac{\pi}{2L}\right)^2} - \frac{1}{3}\cos\frac{3\pi x}{2L}\, e^{-9Dt\left(\frac{\pi}{2L}\right)^2} + \frac{1}{5}\cos\frac{5\pi x}{2L}\, e^{-25Dt\left(\frac{\pi}{2L}\right)^2} + \cdots\right] \tag{31}$$

Jost (1952, p. 35), e.g., has presented an analogous solution for the finite case.

Case III. At time zero the moisture content is uniform throughout the sample and after the experiment begins the evaporation rate decreases in proportion to the evaporable moisture content at the surface, or

$$\begin{aligned} &\text{at } t = 0 \qquad \theta = \theta_o \qquad -L \leq x \leq L \\ &\quad t > 0 \quad a' = c(\theta - \theta_e) \text{ at } x = L \text{ and } -a' = c(\theta - \theta_e) \text{ at } x = -L \end{aligned} \tag{32}$$

wherein a' is the unsteady flux of moisture across the surface. The solution (Newman, 1931) according to Hougen et al. (1940) is of the form

$$\frac{\theta - \theta_e}{\theta_o - \theta_e} = \sum_{1}^{\infty} 2\exp\left(\frac{-Dt}{L^2} B_n^2 A_n^2 \cos\frac{B_n x}{L}\right) \tag{33}$$

wherein A_n and B_n are further defined. Crank (1956, p. 34) gives a

solution of this case in terms of an error function.

Case IV. At time zero the moisture distribution is parabolic--as would be established in drying according to Case I--and the initial boundary conditions can be expressed by

$$t = 0 \quad \theta = \theta_p \text{ from } x = -L \text{ to } 0 \text{ and from } x = L \text{ to } 0. \tag{34}$$

θ_p indicates the parabolic moisture content. According to Hougen et al., Newman (1931) developed an equation of the form

$$\frac{\theta - \theta_e}{\theta_p - \theta_e} = \sum_{1}^{\infty} 2 \exp\left[-\left(\frac{Dt}{L^2}\right) B_n^2\right] A_n \cos\frac{B_n x}{L} - \sum_{1}^{\infty} 2 \exp\left[-\left(\frac{Dt}{L^2}\right) B_n^2\right] B_n \cos\frac{B_n x}{L} \tag{35}$$

All the above solutions are often presented in terms of the average moisture content of the solid at any time during drying, obtained by integrating the above equations over the thickness of the solid, i.e.,

$$\theta_{avg} = \int_0^L \frac{\theta \, dx}{L} \tag{36}$$

For Case II the average moisture content as a function of time is given (Sherwood, 1929a) by

$$\frac{\theta - \theta_e}{\theta_o - \theta_e} = \frac{8}{\pi^2}\left\{\exp\left[-Dt\left(\frac{\pi}{2L}\right)^2\right] + \frac{1}{9}\exp\left[-9Dt\left(\frac{\pi}{2L}\right)^2\right] + \frac{1}{25}\exp\left[-25\,Dt\left(\frac{\pi}{2L}\right)^2\right] + \cdots\right\} \tag{37}$$

wherein L is 1/2 the thickness of the drying slab and the other terms have been previously defined.

When t is large the limiting form of the above equation is (Marshall, 1950)

$$\frac{\theta - \theta_e}{\theta_o - \theta_e} = \frac{8}{\pi^2}\exp\left[-Dt(\pi/2L)^2\right] \tag{38}$$

from which an expression for the rate of drying may be derived to be

$$\frac{d\theta}{dt} = -\frac{\pi^2 D}{4L^2}(\theta - \theta_e) \tag{39}$$

This equation predicts that the rate of drying varies directly with D and $(\theta - \theta_e)$ and inversely with L^2. Equation (38) holds only for $(\theta-\theta_e)/(\theta_o-\theta_e) < 0.6 - 0.7$ (Sherwood, 1929a; Marshall, 1950).

The mathematics of all these solutions is acceptable but one must continuously question the degree to which the drying sample meets the assumptions and the boundary conditions of the mathematical solution. It would appear that employed together, the solutions of Cases I and II would describe a considerable portion of the drying period of an initially saturated sample; even so, the solution of Case II for the falling rate period is limited to the condition of 30 to 40 per cent of the moisture remaining. Sherwood (1929a) considered the physical interpretation of Case II to be consistent with the assumptions (in addition to the general assumptions) that evaporation takes place at the surface and that the resistance to vapor diffusion may be considered negligible. If Sherwood's interpretation of evaporation at the surface is correct for Case II and, if also, the liquid concentration at the surface falls to zero immediately after the start of drying as required by the boundary conditions, a contradiction immediately arises. The contradiction arises from the fact that the two conditions being met simultaneously implies the quite improbable evaporation from a dry surface.

The boundary condition of Case III expressing the proportionality between the evaporation rate and the evaporable moisture at the surface is aesthetically very satisfying and corresponds to the often expressed condition of "unsaturated surface drying." That such a boundary condition really exists is based more on circumstantial than on direct

experimental evidence, however.

Case IV seems a very logical one but has apparently never been applied by soils workers.

The assumption of a constant diffusion coefficient throughout drying is certainly in error. In all the applications of the above solutions the diffusion coefficient has been determined from the data obtained during the drying process; thus a diffusion constant was chosen by fitting the diffusion equation to the data (Van Vorst,[21] p. 8). If the diffusion equation fits the data this procedure yields an average diffusion coefficient representative of the range of diffusivities encountered.

The success of diffusion equations applied to the drying of such materials as wood and clay appears to be due to the general formal similarity of the solutions and their relative insensitivity to deviations from the boundary conditions, and to integration methods which tend to compensate for errors in the assumptions. In spite of objections to their use, diffusion-type equations do yield solutions in reasonable agreement with experiment. This is the justification for their use.

Diffusion equations, concentration-dependent diffusion coefficient.— In view of the voluminous literature on unsaturated moisture flow, the number of excellent recent reviews dealing with unsaturated flow and the solution of the diffusion-type equations wherein the diffusivity varies with the moisture content of the soil (Klute, 1952; Philip, 1955, 1957b, 1957c; Childs, 1956; Crank, 1956; Klute et al., 1956;

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[21] Van Vorst, op. cit.

Soane;[22] Gardner, 1953, 1959a, 1959b), the previous coverage of some of the solutions in the section on the effect of water-table depth on evaporation (see pages 24-29), and the statements already made in discussing diffusion terminology and diffusion-type equations with constant D, this section will be devoted to the theory involved.

The analysis of moisture flow problems involving moisture content-dependent parameters consists of two parts: (i) determination of the moisture conductivity of unsaturated soil as a function of moisture content, and (ii) the solution of certain equations which have the character of diffusion equations with diffusivity dependent upon moisture content (Childs, 1956). The moisture conductivity as a function of moisture content should be and currently usually is determined independently of the data of the particular problem tackled. The development of the equations to be solved (Klute, 1952; Klute et al., 1956; Childs, 1956) is always similar to Gardner's (1959b) treatment: Darcy's law, which is applicable to saturated flow (adsorptive forces are negligible and the potential is made up of gravitational and hydrostatic pressure terms), can be expressed in vector notation by

$$v = -K \operatorname{grad} \Phi \qquad (40)$$

wherein v is the volume flux,

Φ is the potential or hydraulic head, and

K is the hydraulic conductivity.

The application of Darcy's law to unsaturated flow involves replacement of the hydraulic or saturated conductivity K by the capillary or

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[22]Soane, B. D. 1958. An application of a thermodynamic flow equation to water movement in unsaturated soil. M. S. Thesis. Utah State University. Logan, Utah.

unsaturated conductivity k. The latter varies with moisture content. The acceptability of this modification is based on empirical evidence. A unique relationship between moisture content θ and soil moisture potential ψ is assumed. The modified Darcy equation, in one dimension neglecting gravity, becomes

$$v = k\,(\partial\psi/\partial\theta)(\partial\theta/\partial x) = D\,(\partial\theta/\partial x). \tag{41}$$

The product $(k\,\partial\psi/\partial\theta) = D$ has been termed the soil water diffusivity due to its formal analogy with the thermal diffusivity in the equations of heat flow.

Combining the above equation with the equation of continuity yields

$$\partial\theta/\partial t = \nabla D \cdot \nabla\theta = \frac{\partial}{\partial x}\left(D \frac{\partial\theta}{\partial x} \right). \tag{42}$$

This equation for moisture flow has the same form as Fick's diffusion equation but most soils workers consider the formal similarity to be merely coincidental since several mechanisms of unsaturated flow may be operating.

The differential equation for moisture flow in soils is perfectly general. Therefore it is applicable to both the wetting (infiltration or absorption) and the drying (desorption) of soil. The solution for absorption when D is a given function of θ is also the solution for desorption when D is the same function of $(\theta_o - \theta)$ and vice versa (Crank, 1956, p. 270). The solution of the flow equation has most often been obtained for the following boundary conditions:

For infiltration (semi-infinite case), (Crank, 1956, p. 266; Philip, 1957c)

$$\begin{aligned} &\text{at } t = 0 \quad \theta = 0 \quad \text{at } x > 0 \\ &\text{at } t > 0 \quad \theta = \theta_o \quad \text{at } x = 0 \end{aligned} \tag{43}$$

For desorption (semi-infinite case), (Philip, 1955, 1957a, 1957b; Crank, 1956, p. 266; Gardner, 1958, 1959a; Gardner and Fireman, 1958)

$$\text{at } t = 0 \qquad \theta = \theta_o \qquad \text{at } x > 0$$
$$\text{at } t > 0 \qquad \theta = 0 \qquad \text{at } x = 0 \tag{44}$$

wherein θ (for absorption or desorption) is the moisture content at any point x in the sample at time t,

θ_o (for desorption) is the initial uniform moisture content of the soil,

θ_o (for absorption) is the concentration of water at the surface at which water enters the soil, and

$\theta = 0$ (for absorption and desorption) is the moisture content of the soil in equilibrium with the drying conditions.

The desorption case, it will be noted, has the same boundary conditions as Case II of the constant diffusion coefficient section, hence the remarks made there are again applicable. Due to the nature of the field infiltration problem, studies of this process have dealt principally with the seim-infinite case; solutions for the desorption case may be for an infinite (drying at both opposing surfaces of a slab), a semi-infinite (evaporation from one surface of the sample), or a finite system.

The flow equation can be integrated for steady-state flow but for non-steady flow the equation must usually be solved numerically. Methods of solution have been discussed by Crank (1956) and by Van Vorst.[23] Graphical solutions presented by Gardner (1958, 1959a) and

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[23]Van Vorst, op. cit.

especially by Crank (1956) with diffusivity depending on moisture content in various ways show that the solutions are not very sensitive to exact numerical values of D as long as the analytical form of the dependence on θ is correct.

A variety of approximations to the value of D have been made in order to make the mechanics of solution easier (Crank and Park, 1949; Crank and Henry, 1949a, 1949b; Gardner, 1959a) and these can be confusing. Gardner mentions a weighted-mean diffusivity $\overline{D}$; a relative weighted-mean diffusivity $\overline{D}/D_o$ in which D_o is the diffusivity at equilibrium dryness; and D', an average diffusivity which is sometimes treated as a constant for a given flow condition. Gardner points out that for finite media the assumption of a constant average diffusivity is not good because the entire range of water contents and diffusivities is no longer always represented in the medium.

For both adsorption and desorption the diffusivity of soil moisture increases as the moisture content increases. Crank (1956, pp. 276f) points out a number of general conclusions for a system in which D increases as the concentration increases, but is a function of no other variable. These should be of considerable interest to soils workers. They include:

(i) In the early stages of absorption or desorption in a semi-infinite system the amount absorbed or desorbed is directly proportional to the square root of time--a fact which follows from the dependence of concentration on the single variable $x/t^{1/2}$ for the boundary conditions enumerated above.

(ii) When they cease to be linear the absorption and desorption curves

plotted versus $t^{1/2}$ become concave toward the $t^{1/2}$ axis and approach a final equilibrium value asymptotically. This apparently general result lacks a satisfactory, general mathematical proof.

(iii) If D increases as concentration increases the shape of the absorption curve is often not significantly different from the corresponding curve for constant D. Crank considers this to be consistent with the absorption curves being linear versus $t^{1/2}$ over most of their length. Desorption curves plotted versus time are much more sensitive to the form of D, if D increases as concentration increases. The desorption curves are not linear versus $t^{1/2}$ for as large a value of the fractional sorption[24] as are the absorption curves.

(iv) When D increases as concentration increases through the relevant range of concentration, desorption is always slower than absorption. The reverse is true if D decreases as concentration increases.

The above statements, particularly (i) and (iii), indicate that the desorption process is much more difficult to recognize and analyze empirically than is infiltration. This probably accounts for the historically greater emphasis on the infiltration of water into soil than on the drying of soil.

A number of important practical problems have been clarified through the solution of the concentration-dependent diffusivity form of the moisture flow equation. The utilization of this approach is not a cure-all for soil moisture studies, however, since:

(i) Solution of the equation requires a knowledge of the relation

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[24]Sorption is used as a general term which includes both adsorption and desorption. Adsorption is occurring if there is a net gain of adsorbate by the medium; desorption is occurring if the net change in the amount of adsorbate is in the direction of decreasing amount in any arbitrary time period.

between D and θ. This requires determination of (a) the capillary conductivity k as a function of moisture content θ, and (b) the moisture retention curve (or moisture characteristic) of the soil in question. (The quantity $\partial \psi / \partial \theta$ in the definition of D is the slope of the moisture retention curve.) The range of moisture potential over which these quantities can be determined is limited by measurement techniques; in addition, the procedures are lengthy and laborious. Therefore, most soils have not been thus characterized.

(ii) Solutions of the flow equation for the analytical forms of the relation between D and θ may not be readily available. Then, too, numerical solutions can be tedious.

(iii) Solutions apply only to soil profiles that are relatively homogeneous with respect to texture and structure. Many soils of interest exhibit profile development, the various soil horizons of which possess physical characteristics markedly different from each other.

(iv) Present solutions are applicable only to either the period of constant rate of evaporation (steady state evaporation), or to a portion of the first falling rate period because only liquid phase flow is considered. About the only constant rate of evaporation case which occurs naturally for extended periods of time is that of evaporation from shallow water-tables. During the falling rate period the solutions fail when the diffusion of water vapor becomes evaporation rate-controlling.

(v) Normal non-isothermal conditions cannot be treated exactly, and the analysis is again inapplicable if temperature effects on flow predominate over liquid flow.

(vi) Both hysteresis and volume changes are neglected.

The above reasons are justification enough for continuing to search for methods of analysis which are either (a) more generally applicable to soil moisture movement than the diffusion-type equations for liquid phase flow, or (b) able to handle specific situations better or easier than the present moisture flow equations can.

Simultaneous flow of heat and moisture

The Philip and De Vries approach.--Moisture transfer under temperature gradients is very slight in both very dry and very wet soil. The transfer is a maximum at some intermediate moisture content which seems to depend on both the soil moisture potential and the air-filled pore space (Philip and De Vries, 1957). Moisture movement in the moisture range wherein temperature gradients have a marked influence on moisture flow has been studied by Bouyoucos (1915), Winterkorn (1947), Smith (1944), Gurr et al. (1952), Taylor and Cavazza (1954), and others. In all these studies a net accumulation of water at the low temperature end of the samples was observed. This characteristic result has usually been explained in terms of the excess of flow in the vapor phase toward the cold end of the sample, over the return liquid phase flow toward the warm end. However, the magnitude of the moisture movement was in no cases explicable on the basis of vapor diffusion theory adjusted to take into account the reduction of diffusion cross-section by the solid matrix, the moisture content, and the tortuous path of flow. The simple diffusion theory predicts a moisture flow smaller than the observed flow by a factor of about ten.

Philip and De Vries (1957) attacked this situation with an

admittedly approximate analysis in which they attempted to take into consideration the interaction of the vapor, liquid, and solid phases, and the difference between the average temperature gradient in the air-filled pores and in the soil as a whole. These inclusions in their analysis helped to bring the predicted magnitude into better agreement with the experimental results. The moisture diffusivity in the vapor, liquid, and adsorbed phases was introduced by using a moisture content dependent diffusivity D* (Philip 1955, 1957c) defined by

$$D^* = D_{liq} + D_{vap} + D_{ads} \tag{45}$$

wherein

D_{liq} is the diffusivity of water in the liquid phase,

D_{vap} is the diffusivity of water vapor, and

D_{ads} is the diffusivity of water in the adsorbed phase.

Each of the diffusivity components can be further subdivided into thermal contributions and moisture content contributions as follows:

$$\begin{aligned} D_{liq} &= D_{T\,liq} + D_{\theta\,liq} \\ D_{vap} &= D_{T\,vap} + D_{\theta\,vap} \\ D_{ads} &= D_{T\,ads} + D_{\theta\,ads}. \end{aligned} \tag{46}$$

The D_{ads} component of diffusivity is derived from the de Boer (1953) model of an ideal, two-dimensional gas (Philip, 1955, appendix I). This component has not been applied in practice. It has been either ignored or considered a minor contributor to D_{vap}. We shall not consider it further.

The other consideration included in the theory of Philip and De Vries, the ratio of the average temperature gradient in the air-filled pores to the overall temperature gradient, is obtained (De Vries, 1952a,

1952b), according to Philip and De Vries (1957), by treating the soil as a continuous medium (water or air) in which "particles" of water or air are randomly dispersed.

> On the basis of certain plausible assumptions about the shape of these particles, values of the ratios between the average temperature gradients in the particles and in the medium can be computed from their respective thermal conductivities.

Philip and De Vries (1957) present tabular values of this temperature ratio for various combinations of moisture content and porosity, at a temperature of 20° C. The ratio of the average temperature gradient in the air-filled pores to the overall temperature gradient for these conditions ranges from 1.4 to 3.0. De Vries and Philip (1959) emphasize that the fine structure of the temperature field may differ in important particulars from the fine structure of the vapor field, since boundary conditions governing transfer are quite different in the two cases.

Philip (1957a) and Philip and De Vries (1957) treated the data of Moore (1939) according to the above theory. Their analyses indicate that for the Yolo loam soil studied, the moisture diffusivity (D_θ) is indistinguishable from the vapor moisture diffusivity (D vap) at moisture potentials greater than 10^5 cm water ($\sim$98 bars suction) and indistinguishable from liquid moisture diffusivity (D liq) at moisture potentials less than 10^4 cm water ($\sim$10 bars suction). The thermal moisture diffusivity (D_T) was indistinguishable from the thermal vapor diffusivity (D_T vap) at moisture suctions greater than about 13 bars. These workers concluded that experimental methods to distinguish between liquid and vapor transfer have not done so because what has been supposed to be vapor flow has actually been predominantly a discontinuous

sequence of vaporizations and condensations. For example, moisture could vaporize from the liquid film on one side of a pore and condense on the other side of the pore under the influence of a temperature gradient. Such a mechanism appears realistic in view of the solid-water-gas geometry of the soil system. It is very difficult to substantiate experimentally, however.

Thus far, thermal influences on moisture flow have been considered, but the thermal properties of soil (Richards et al., 1952) must also be considered since heat and moisture are simultaneously transferred when there is a temperature gradient. De Vries has been the modern leader in this field (1950a, 1952a, 1952b, 1952c, 1958) but there are other major contributors (e.g., Patten, 1909; Kersten, 1949).

Heat transfer in moist soil is due mainly to heat conduction through the soil particles and the adhering water. The air-filled pores also contribute to the conduction of sensible heat but a more important contribution is to the heat transfer by evaporation-condensation sequence. The heat transfer caused by vapor diffusion accompanied by condensation causes an increase in the thermal conductivity. The apparent thermal conductivity is defined (De Vries, 1950) by

$$C_{Ta} = C_T + C_{Tv} \qquad (47)$$

wherein C_T is the real thermal conductivity (cal sec^{-1} cm^{-1} $^oC^{-1}$), and

C_{Tv} is the vapor contribution to thermal conductivity.

C_{Ta} is the thermal conductivity found experimentally. The most striking feature of C_{Tv} is its rapid increase with temperature. De Vries reports its temperature coefficient as 0.059 $^oC^{-1}$ as compared with the temperature coefficient of C_T of 0.0015 $^oC^{-1}$.

Krischer and Rohnalter (1940) measured the diffusion coefficient of saturated water vapor through air under the influence of a temperature gradient and found that the data could be represented by

$$D_{atm} = 4.42 \times 10^{-4} \left(T^{2.3}/P_a\right) \tag{48}$$

in the temperature range 20 to 70° C. In equation (48) T is the absolute temperature and P_a is the total atmospheric pressure expressed in millimeters of mercury.

Philip and De Vries (1957) used the following values of thermal conductivities, in cal cm^{-1} sec^{-1} $^oC^{-1}$ at 20° C, in their analysis: soil minerals--7×10^{-3}; quartz--20×10^{-3}; air--0.0615×10^{-3}; and water--1.42×10^{-3}. The relatively much lower thermal conductivity of air causes temperature changes in the soil pores to lag behind those of the soil matrix and results in pronounced temperature gradients across narrow air spaces. The low thermal conductivity of air is the main factor causing the ratio of temperature in the air-filled pores to that of the bulk soil to be as large as 3.0.

Philip and De Vries (1957) present the general differential equation describing moisture movement in porous materials under combined temperature and moisture gradients for one-dimensional vertical flow as follows:

$$\frac{\partial \theta}{\partial t} = \nabla \cdot (D_T \nabla T) + \nabla \cdot (D_\theta \nabla \theta) - \frac{\partial k}{\partial z} \tag{49}$$

wherein θ is moisture content,

t is time,

T is absolute temperature,

D_T is the thermal diffusivity, D_T liq + D_T vap,

k is the capillary conductivity of the soil,

z is the vertical space coordinate, and

D_θ is the moisture diffusivity, D_θ liq + D_θ vap.

The heat conduction equation for soil is given similarly as

$$C_v \frac{\partial T}{\partial x} = \nabla (C_{Ta} \nabla T) - H_L \nabla (D_\theta \text{ vap } \nabla \theta) \qquad (50)$$

wherein C_v is the volumetric heat capacity of the soil (cal cm^{-3} $^oC^{-1}$),

C_{Ta} is the apparent thermal conductivity of the soil (cal sec^{-1} cm^{-1} $^oC^{-1}$), and

H_L is the latent heat of vaporization of water.

Both the above equations are of the diffusion type involving θ- and T-dependent diffusivities as well as gradients of both θ and T. The equations (49) and (50) govern the simultaneous moisture and heat fields in soils. Their simultaneous solution is yet to be accomplished.

De Vries (1958) generalized the above equations by making a distinction between changes of moisture content in the liquid and vapor phases. He discusses in detail the interaction between heat and moisture transfer in steady state heat conduction. He found that the behavior depends on the boundary conditions for moisture transfer, on the direction of the temperature gradient, and on the ratio of the two moisture diffusivities entering the analysis.

Solution of the differential equations (49) and (50) or even the more approximate analyses made by Philip and De Vries (1957) and by De Vries (1958) require not only detailed characterization of the moisture characteristics of the soil but also of its thermal properties.

Many of the parameters employed are difficult to determine accurately. Although solution of the simultaneous heat and moisture fields in soils is

> ...at present, a very difficult task, its solution is worth great pains, since it is crucial to our understanding of the microclimatology and microhydrology of bare soils. (Philip, 1957a)

The approach of Henry.--Workers in the textile industry are very much interested in the propagation of humidity and temperature in fabrics. The general problem is that of the transfer of moisture or water vapor through a porous body which may absorb (or release) moisture with the evolution (or absorption) of heat. Thus the analyses of the simultaneous transfer of heat and moisture in textiles should be directly applicable to another inhomogeneous, porous, absorbent material--soil.

Henry (1939, 1948) demonstrated that in the diffusion of humid air the accompanying thermal effects result in a coupled diffusion of moisture and heat. Henry showed that the combined diffusion processes can be considered mathematically equivalent to the independent diffusion of two quantities each of which is a linear function of both vapor concentration and temperature. Henry cited the classical coupled vibration problem as his model analogy. We consider here only the basic equations of the treatment and some pertinent conclusions from the experimental application of the theory. These are taken from Crank (1956, chpt. 13).

If moist air is diffusing into an element of a textile package two equations can be derived, one expressing the rate of change of moisture concentration and the other the rate of change of temperature.

The moisture concentration changes according to (i) diffusion of vapor through the air pores and through the fibers, and (ii) by absorption or desorption of moisture from the air pores by the fibers. Letting v be the air-filled porosity of the textile package and (1 - v) the fraction occupied by fiber of density ρ_s, the equation expressing vapor flow can be written

$$v\, g\, D_{atm} \frac{\partial^2 C}{\partial x^2} = v \frac{\partial C}{\partial t} + (1 - v)\ \rho_s\ \frac{\partial M}{\partial t} \tag{51}$$

wherein C is the concentration (gm cm^{-3}) of water vapor in the air pores, M is the mass fraction of moisture in the fiber, D_{atm} is the diffusion coefficient of water vapor in air, and g is a tortuosity factor.

Similarly, the temperature changes occurring in the element result from (i) conduction of heat through the air and the fibers, and (ii) heat evolved on absorption of moisture by the fibers. These considerations are expressed mathematically by

$$c\rho \frac{\partial T}{\partial x} = C_{Ta} \frac{\partial^2 T}{\partial x^2} + q\ \rho \frac{\partial M}{\partial t} \tag{52}$$

wherein c is the specific heat of the fibers (cal gm^{-1}), C_{Ta} is the apparent thermal conductivity of the package, ρ is the bulk density of the package, and q is the heat of absorption per gram of water absorbed. Both equation (51) and equation (52) contain M, the amount of moisture contained in the fibers. This illustrates that the transfer of moisture and of heat are coupled. Henry (1948) showed, however, that simplifications are possible when (a) the coupling is either very strong or very weak, (b) the two elementary diffusions occur at very different rates, or (c) analysis is made of changes in only one of the

variables.

The analysis of Henry (1948) for the diffusion of humid air into compressed cotton fibers over a range of temperatures and humidities indicated that: At 20, 50, and 80° C the "isothermal" moisture diffusion coefficient D_θ is much smaller than, about the same magnitude as, and 1 to 3 times, respectively, the "constant vapor concentration" thermal diffusion coefficient D_T. The interaction diffusion coefficients corresponding to the "normal co-ordinates" of the coupled vibration problem "are always such that one is greater and the other less than either of the diffusion constants which would be observed for the moisture and heat, were these not coupled by the interaction." (Henry, 1948)

The theory of Henry has been modified and applied to the study of propagation of temperature changes resulting when air is forced through the hollow core of wool-packed cylinders (Cassie, 1940; Cassie and Baxter, 1940). The theory predicts that the temperature change is propagated through the textile in two stages. One part of the total temperature should pass through the textile at the same speed as the air and the other part at roughly 2.5×10^{-4} times this speed. The assumptions made in deducing the mathematical equations imply that there is a sharp front between the regions of unchanged and changed moisture content of the textile. Thus Cassie interpreted the slow component as representing the propagation of the change in moisture content; the fast component he considered to represent the propagation of temperature and water vapor exclusive of changes in moisture content. Cassie and Baxter report results obtained in passing air at 1.4 cm sec^{-1}

through a cylinder of wool with one cm-thick walls. They found the fast temperature wave to be propagated at 1.4×10^{-2} cm sec^{-1} whereas the slow component moved at 5.7×10^{-4} cm sec^{-1}. At these velocities the temperature waves would have traversed the wall thickness in 70 seconds and 30 minutes, respectively.

All the above applications of Henry's theory have been to water vapor absorption at vapor pressure ratios of 0.3 to 0.7. The textiles were therefore very dry and liquid phase moisture flow was undoubtedly slight. Preston (1948) did not use Henry's theory but he did report observations made during the drying of textiles when the moisture content exceeded "the usual saturation values of water vapour." He found that there are two large and distinct temperature waves which travel through a moist textile during drying.

> At any point in the material, there is first a rise, then a fall and, finally a second rise of temperature, as the two temperature waves travel successively from the hot side towards the cool one.

On the basis of several considerations Preston interpreted these results as indicating that

> ...the first temperature wave we observed was caused by a cycle of distillation and condensation processes. In these, vapour moves away from, and liquid towards, the source of heat. The extraction produced by the latter part of the cycle causes the migration of solute towards the source of heat. As the material dries through the transfer of moisture away from the source of heat the distance the liquid has to travel lengthens, there is an increasing resistance to the maintenance of this cycle and diffusive heat-transfer must operate alone. These require a greater temperature difference for a given rate of heat transfer. There is thus a fall of temperature as the heat is being removed on the cooler and damper side by an additional and easier mechanism. When finally the material dries throughout, the liquid-vapor heat-transfer mechanism previously operating on the cooler side of the material is eliminated and the temperature rises once more.

The general agreement among Preston's observations and those of Cassie et al. (1940) and Henry (1939, 1948) along with the parallelism of effects of temperature gradients on moisture flow in textiles and soils (Philip and De Vries, 1957) suggest the possible applicability of Henry's theory to soils. It has never been applied to soils, however.

Irreversible thermodynamics.--Classical thermodynamics or the thermodynamics of the equilibrium state is not applicable to the simultaneous transfer of heat and moisture, but the recently developed irreversible thermodynamics (Prigogine, 1955) or the thermodynamics of the steady state is. Hutchinson et al. (1948) give the fundamentals of the theory as follows:

> By analogy with the dynamics of mechanical systems, it is necessary, in order to develop a true "thermodynamics" to introduce velocities and forces. Thus, if a flow of heat is taking place at a rate J_1 it may be regarded as due to a thermal "force" X_1, which is dependent on the gradient of temperature. Similarly, a flow of matter at a rate J_2 is due to a "force" X_2, which is dependent on the gradient of chemical potential. If both flows take place simultaneously in the same system it may be supposed, in the absence of evidence to the contrary, that the flow rates J_1 and J_2 each depend on both of the forces X_1 and X_2. This is a more general assumption than its converse (i.e., that J_1 depends only on X_1, J_2 on X_2), and effects such as the thermo-osmosis and thermal diffusion depend, in fact, on the flows J_1 and J_2 not being independent.
>
> As a first approximation, it is assumed that the flows are linear functions of the forces:

$$J_1 = L_{11}X_1 + L_{12}X_2$$

$$J_2 = L_{21}X_1 + L_{22}X_2 \qquad (53)$$

The rate of creation of entropy S' for spontaneous processes is always expressible as a sum of a number of terms (one for each process). Each of these terms is the product of two factors such that the rate of energy dissipation TS' is expressed by (Eckart, 1940)

$$TS' = \sum_i (j_i x_i), \qquad (54)$$

To continue with Hutchinson and co-workers,

> ...the factor j_i can be chosen as equal to J_i, the rate of flow, or displacement, of heat, matter, etc. By analogy with the relation, work = displacement x force in mechanics, the factors x_i are therefore identified as the "forces," X_i, which give rise to the flows or displacements. Moreover the theory gives the explicit expressions for these forces in terms of the gradients of temperature, chemical potential, etc.

Use of the expressions such as (54) make equation (53) applicable to particular problems.

Cary[25] has developed the equations

$$J_{H_2O} = - L_{H_2O} C_p \ln \frac{T^h}{T^c} + (\xi + M L_{H_2O}) \left(\frac{1}{T^c} - \frac{1}{T^h} \right) \qquad (55)$$

$$J_{Heat} = (L_{Heat} + \xi M) \left(\frac{1}{T^c} - \frac{1}{T^h} \right) - \xi C_p \ln \frac{T^h}{T^c} \qquad (56)$$

to apply to water movement in soil under a thermal gradient. In equations (55) and (56) C_p is the heat capacity of water, T^h and T^c are respectively the temperatures of the hot and cold ends of the soil column, M is an integration constant, ξ is the coefficient of interaction between heat and moisture flow, and the other terms are directly analogous to those previously defined. Cary has obtained experimental results in good agreement with the predictions of the theory.

The advantages of the irreversible thermodynamics approach are that it is capable of handling the simultaneous occurrence of two or more processes, it avoids in a large measure the detailed characterization of the sample material that is required by more mechanistic approaches, and it yields an evaluation of the interaction coefficients. It has associated with it certain disadvantages, however, including:

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[25]Cary, J. W. 1959. Unpublished report. Utah State University. Logan, Utah.

(a) theoretical reservations concerning its application to reactions very far removed from equilibrium and the assumption that the flows are linear functions of the forces, (b) the requirement of detailed knowledge of the forces and their space distribution, and careful measurement of the fluxes corresponding to all the forces assumed, (c) the fact that the results are very much a function of the system studied with the consequences that the method is not absolute and that direct comparison between different systems or extrapolation of results from one system to another very different one must be made with caution.

The above considerations make it difficult to predict how valuable irreversible thermodynamics will prove to be in soils research.

Conclusions from Review of Literature

1. Analyses of evaporation have dealt mainly with the mass transfer process, while the accompanying heat transfer process has been largely ignored. Heat transfer is logically the first limiting step, however, in evaporation from free water or wet soil because it determines the availability of vapor for transport.

2. Detailed knowledge of the evaporation process has been hampered by difficulties in determining the thickness of the laminar layer next to the surface and the actual temperature of the surface.

3. The Dalton equation is empirical and cannot be expected to apply to conditions varying much from the experiments which yielded it. Empirical evaporation equations are often of the Dalton law type, but the parameters in the equations may bear little relationship to those of the original formulation.

4. Evaporation from free water or moist surfaces exhibits a power dependence on windspeed. Present methods of measuring windspeed are of doubtful value.

5. Wet-bulb depression is probably the most useful single index of evaporation from a moist surface since it integrates the effects of temperature, humidity, and windspeed into a single measurement. There is no correspondingly useful index of evaporation from soil if a dry layer has formed at the surface; here the rate of evaporation is a function of the properties of the medium as well as the external conditions.

6. A mulch of dry soil a few millimeters in thickness is effective in reducing evaporation since the rate of diffusion of the water vapor

through the mulch becomes the limiting process.

7. The evaporation rate is of the order of 100 times as sensitive to mulch thickness as to water-table depth. Evaporation versus either depth of mulch or depth to the water-table will often yield a linear plot on log-log paper; this form is in qualitative agreement with simple vapor diffusion theory.

8. Mechanistic analyses of moisture and heat flow in soils require detailed characterization of the moisture and thermal properties of the material. Obtaining the information is laborious and the accuracy of the values is often in question.

9. The simultaneous flow of heat and moisture has not as yet been satisfactorily resolved.

10. Analyses of drying based on capillary theory are able to describe the process only in coarse materials. Even for these, the analyses break down as soon as the moisture films become discontinuous.

11. Empirical methods of analysis of drying have not enjoyed the same popularity as for the wetting of soil. The reason lies partly in the peculiarities of unsaturated flow when the diffusivity increases as the moisture content increases, as it does for soil.

12. The usual boundary conditions assumed in solving the moisture flow equation approximate the actual conditions of infiltration much more closely than the equivalent boundary conditions approximate the actual boundary conditions of drying.

13. The development of a parabolic moisture distribution during drying appears to be characteristic of fine-textured, porous materials with appreciable colloidal character.

14. Improvements must be made in methodology if trustworthy measurements of vapor pressure gradients within a drying soil profile are to be made.

15. Soils workers have given little direct attention to evaporation as a function of the moisture distribution.

16. Two schools of thought have arisen concerning the concept of diffusion. One school adheres to the classical definition of diffusion as a process which leads to equalization of concentrations within a single phase. The other school of thought considers the process loosely as one of diffusion if the mathematics of diffusion applies. In terms of unsaturated moisture flow, adherents of the "classical" school of thought consider only vapor transfer to be a diffusion process. The other school of thought makes no attempt to define diffusion.

17. The mathematics of diffusion is the most successful method to date for describing isothermal unsaturated moisture flow.

18. The time dependence of moisture removal from soil is independent of the "driving force" which initiates and maintains flow and of the flow geometry. This together with a consideration of the cause of unsteady state unsaturated flow indicates that submicroscopic (molecular) flow processes dominate the macroscopic moisture flux.

19. The multitude of interacting forces in the multiphase soil system prevents unequivocal interpretation of the mechanism of moisture flow.

20. Although the temperature dependence of evaporation, transpiration, and moisture flow has been studied empirically, there are apparently no applications of reaction rate theory to the drying of soil.

THEORY OF SOIL DRYING

There are several possible rate limiting or "master" processes in the evaporative drying of soil. These include the supply of heat to the site of evaporation, the transfer of water vapor through the soil and the atmosphere, and the unsaturated flow of moisture within the soil. Quantitative description of the drying of soil from saturation to equilibrium dryness is complicated, however, because the same master process may not be limiting during the whole time.

Methods of analysis of drying have included vapor diffusion theory, solution of the diffusion-type equation for liquid moisture flow, capillary flow theory, and engineering-type mass and heat transfer concepts. Each of these approaches is capable of treating only one of the possible rate controlling transfer processes. Therefore, such analyses accurately describe the phenomenon only if the assumed process is rate limiting. This situation indicates that these methods used singly are inadequate for describing the entire moisture range encountered in drying and that new approaches to studying drying might be profitable.

Drying is a rate process. Therefore, it appears worthwhile to apply the principles of chemical kinetics which "deals with the rate of chemical reaction, with all factors which influence the rate of reaction, and with the explanation of the rate in terms of the reaction mechanism" (Frost and Pearson, 1953, p. 1) to the evaporative loss of moisture from soil. This approach, besides utilizing macroscopic measurements on the system studied, can call upon the detailed theories of statistical mechanics and kinetic-molecular theory for understanding microscopic phenomena. This versatility of kinetics lends to its appeal.

Some of the more interesting applications of kinetic or rate process theory have been to molecular diffusion in silicates (Barrer and Jost, 1949; Barrer and Rees, 1954; Palmer[1]) water vapor diffusion through copolymers (Kumins, et al., 1957), pressure effects on rates of ionic reactions (Burris and Laidler, 1955), migration processes in solids (Seitz, 1948; Vineyard, 1957; Ubbelohde, 1957), viscous flow and diffusion in liquids (Glasstone, et al., 1941), and flow of vapors through micropores (Carman and Raal, 1951). The only applications to moisture flow in soils appear to be those of Biggar[2] and John[3]. Biggar applied kinetic theory to infiltration of water into soil. John considered moisture flow in steady state evaporation to be a surface diffusion process (Carman, 1956), but did not utilize rate theory extensively.

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[1]Palmer, J. 1956. The kinetics of sorption of amines in montmorillonite. M. S. Thesis. Utah State University. Logan, Utah.

[2]Biggar, J. W. 1956. On the kinetics of moisture flow in unsaturated soils. Ph. D. Thesis. Utah State University. Logan, Utah.

[3]John, P. T. 1958. Vapor pressure gradient and water movement in the top layers of soil. Ph. D. Thesis. University of Washington. Seattle, Washington.

Chemical Kinetics

The chemical kinetics to be applied to the study of the drying rate consists of (i) following the drying process as it proceeds with time at a given temperature, then expressing the results by a rate equation, (ii) repeating the experiments at a series of temperatures so that the temperature dependence of the drying rate can be obtained, and (iii) relating the temperature dependence to the energetics of the reaction.

The above three steps in utilizing chemical kinetics emphasize the flow of moisture in drying since this is the "reaction" that is manifest. However, according to the definition of Frost and Pearson (1953), besides considering the reaction rate per se kinetics embodies a consideration "of all factors which influence the rate of reaction." Since the phase change in vaporization of soil moisture is a large "built-in" energy sink in the drying process, transfer of energy as well as mass must be considered as a factor influencing the drying rate.

The third consideration in kinetic analysis is the mechanism of reaction. For the present study we consider that superficially, at least, the major flow processes are (i) energy--in response to a temperature gradient with the magnitude of flow a function of the thermal properties of the soil, (ii) moisture--(a) as vapor by molecular diffusion within the soil and by eddy diffusion above the soil surface, and (b) as liquid by some type of surface phase flow affected by film thickness and aided by surface migration of molecules. These various aspects of drying are considered further.

Rate equations for moisture flow

Literature findings (see pp. 62-63) indicate that the equation

$$Q = a\, t^b \tag{25}$$

or its linear form

$$\log Q = \log a + b(\log t) \tag{25a}$$

wherein Q is the quantity of water evaporated, a and b are constants, and t is time should fit the drying of soil. This equation has been used extensively in the analysis of infiltration of water into soil (Swartzendruber and Huberty, 1958). It has a sound theoretical foundation in the solution of the unsaturated moisture flow equation as a power series in $t^{1/2}$ (Philip, 1957c; Watson, 1959). If unsaturated moisture flow is limiting the rate of drying, b in equations (25) and (25a) has the value 0.5 (Crank, 1956).

In more standard chemical kinetics terminology, the zero and first order rate equations of Fisher (see eqs. 20 and 21, p. 60) for the drying of soil suspended over sulphuric acid inside desiccators might express the drying of soil columns and field soil profiles. The equations are

$$-d\theta/dt = k^o \tag{20}$$

and

$$-d\theta/dt = \theta\, k' \tag{21}$$

wherein θ is a measure of the total moisture content of the system,

t is time, and

k^o and k' are the zero and first order rate constants.

As implied by its form, equation (20) will apply if the rate of evaporation is independent of the soil moisture content. On the other hand, equation (21) can apply only if the rate of evaporation is moisture content dependent.

On integrating between time zero and the time in question and rearranging one obtains for equations (20) and (21)

$$(\theta_o - \theta) = k^o t \tag{20a}$$

and $$\log \theta_o - \log \theta = (k' t)/2.303 \tag{21a}$$

where for this study $(\theta_o - \theta)$ is the cumulative evaporation in grams of water Q. The zero and first order rate constants k^o and k' can be obtained readily by least squares analysis of the data.

Temperature dependence and the energetics of drying

The Arrhenius equation

$$d(\ln k)/dT = E^*/RT^2 \tag{57}$$

satisfactorily expresses the temperature dependence of the rates of many chemical and some physical processes provided the temperature range is not too large. If the energy of activation E^* is constant with respect to temperature, integration of equation (57) yields

$$\ln k = -E^*/RT + \text{constant, or } k = A \exp(-E^*/RT) \tag{58}$$

wherein k is the rate constant,

A is an adjusting factor termed the 'frequency factor' by Glasstone et al., (1941, p. 1),

R is the universal gas constant, and

T is the absolute temperature.

As indicated by equation (58), E^* may be obtained by plotting log k versus 1/T. The slope of such a plot times (2.303)(R) yields E^*. Throughout this work values of the activation energy obtained in this way will be designated the "experimental activation energies" or the "apparent activation energies."

The energy of activation is associated with an "energy barrier." In endothermic reactions the energy barrier must be at least as large as

the heat absorbed in the reaction. According to the transition state theory of Glasstone and co-workers (1941) the energy barrier is the highest point of the most favorable reaction path on the potential energy surface between the reactants and products.

Activation energies are justifiably calculated only for reactions whose mechanism can be interpreted on the molecular level. On this level, the net process of evaporation of water consists of the escape from the surface of those water molecules which attain sufficient energy to do so, and the incidental return of a certain proportion of them to the surface. Drying of soil occurs only if the number of molecules permanently escaping from the adsorbed moisture films exceeds the number which return to the surface. There is apparently no activation energy associated with the molecules which recondense (Barrer and Rideal, 1935). The energetics of the net evaporation process is then dominated by the molecules which permanently escape. Since the dominant energy sink in evaporation is that of the phase transition, the energy barrier to evaporation of water should be commensurate with the latent heat of vaporization of water.

Unsaturated moisture flow can also be viewed as a molecular process. The fact that unsaturated flow of moisture is not directly proportional to the external driving force (see Table 1, p. 62) can be interpreted as implying that energy barriers to the microdynamic flow processes limit the macroscopic flux. Energy barriers to the microdynamic flow process can be expected to give rise to activation energies when the Arrhenius theory is employed.

The drying of the extremely complicated soil system is dealt with here. It is explicitly stipulated that for the activation energies to

be physically meaningful they must be associated with the rate limiting aspect of the drying process. However, for the soil system and the phenomenon of drying the rate limiting process is not known. The activation energies offer one clue that can be used to identify the limiting process or processes. If this can be accomplished, the way is open for a more detailed analysis of the mechanism of the limiting process.

Since this is a pioneering study, the path is uncharted and methods of circumventing gaps in knowledge and other obstacles are invented at the risk of error. With this understanding the following assertion is made in the interest of providing "reference" values of energy barriers as guides to reasoning: The possible rate limiting physical processes are themselves temperature dependent and, therefore, provide the desired reference values. Thus the ΔH_{vap} of free water, the diffusion of water vapor through air, and the viscosity of water yield upper limits for the energy barriers associated with the processes for which these properties could be rate limiting. It is realized that the values of some of these activation energies could be quite different for soil moisture but the values are considered to be good first approximations and useful as guides.

In applying this thinking one considers, for example, that if analysis of the data yields an activation energy greater than ΔH_{vap} water (about 10.5 kcal $mole^{-1}$ at room temperature), the evidence is that something with an activation energy greater than that of evaporation of water is rate limiting. Experimental activation energies can also be obtained from the falling rate period of drying when hypothetically unsaturated flow of moisture to the site of evaporation is rate limiting;

here, if laminar unsaturated surface-film flow is assumed, a reference activation energy is available since the temperature dependence of the viscosity of water is known.

As a review of this type of reasoning the work of Glasstone, Laidler, and Eyring (1941) can be considered. These authors base their discussion of liquids on the concept that by analogy with gases, liquids can be regarded as made up of "holes" moving about in matter. According to this interpretation, the work done in creating holes is of particular importance in the processes of vaporization, viscous flow, or self-diffusion of the liquid. These workers state (p. 491): "The work required to make a hole of molecular size is equal to the energy of vaporization...." Therefore, since $\Delta E_{vap} = \Delta H_{vap} - RT$ where ΔH_{vap} is the normal latent heat of vaporization and RT is the correction for the work done on the external system in vaporizing one mole of the liquid one can quickly estimate the ΔE_{vap} of many substances from readily available ΔH_{vap} information.

The energy barrier for viscous flow of liquids can be thought of as consisting of parts associated with the energy required for the creation of the hole and that associated with the movement of the molecule into the hole. For many nonassociated liquids the ratio of $\Delta E_{vap}/E^*_{vis}$, where E^*_{vis} is the activation energy obtained from the experimentally observed temperature dependence of viscosity η has a value of 3 to 4. For such substances the temperature dependence of viscosity is expressed by an equation of the form

$$\ln \eta = A/T - B \qquad (59)$$

(Prutton and Maron, 1956, p. 105) in which T is the absolute temperature, and A and B are constants. Based on International Critical

Table data and the assumption that equation (59) is valid for water, a value of E^*_{vis} of 4.00 kcal mole^{-1} for the temperature range 10 to 40° C has been calculated. The parameter B in equation (59) is temperature sensitive, however, for the associated liquid water. Glasstone and co-workers (1941, p. 505) give E^*_{vis} water at 0 and 50° C as 5.06 and 3.42 kcal mole^{-1}, respectively.

Glasstone et al. (1941) also consider liquid-liquid diffusion a unit flow process requiring space. They report (p. 525) a value of $E^*_{l\text{-}diff}$ of 5.30 kcal mole^{-1} for heavy water into normal water based on a temperature dependence of the diffusion coefficient of the form $D = A \exp(-E^*/RT)$.

The experimental activation energies of vapor pressure and of the diffusion coefficient of water vapor through air have also been calculated. These values along with those mentioned above are grouped together in Table 2 for ready reference. Most of the results are for the 10 to 40° C temperature range since that is the range of temperature covered in the present study. The experimental activation energies obtained from the temperature dependence of the property in question (these all have asterisk superscripts) are small with the exception of the vapor pressure of water. It is equal the average latent heat of vaporization of water for the same temperature range. This is in agreement with the Clausius-Clapeyron equation which is used to predict the latent heats of vaporization of liquids from the temperature dependence of their vapor pressure.

The second source of data available for comparison with the results of the present theory are those reported in, or calculable from, the literature. Data for this purpose are available from a variety of

experiments including evaporation from free water, transpiration from plants, moisture flow in soil, the drying of wood, evaporation from soil, and kinetics of sorption experiments. Even if the idea of using the "reference" values for the activation energies associated with the possible rate limiting processes of drying proves to be a failure, enough information may still be at hand from the literature findings to interpret the results of the present study in a meaningful way, i.e., through a careful comparison of similarities and dissimilarities of the systems studied and their corresponding activation energies. A list of values of activation energies obtained from the mentioned studies of transpiration, evaporation, and drying are given in Table 3.

Table 2. Reference values of thermodynamic functions and of activation energies for various properties of water and water vapor as obtained from handbook data of their temperature dependence or from experiments on pure water systems.

Property[a]	Energy (kcal mole^{-1})	Symbol	Temperature or temp. range (°C)	Reference (for data or energy)
Latent heat of vaporization	10.49	ΔH_{vap}	10-40	Handbook Chem. and Phys.
Energy of vaporization	10.18 9.61	ΔE_{vap}	0 50	Glasstone et al., (1941, p. 505)
Viscosity of water	4.00 5.06 3.42	E^*_{vis}	10-40	Inter. Crit. Tbls.; Glasstone et al., (1941, p. 505)
Vapor pressure of water	10.58	E^*_{vp}	10-40	Handbook Chem. and Phys.
Water-water self diffusion coeff.	5.30	$E^*_{l\text{-}diff}$	?	Glasstone et al., (1941, p. 525)
Diffusion coeff. water vapor through air	1.06	$E^*_{atm\text{-}d}$	10-40	Inter. Crit. Tbls.

[a]All values are based on a total pressure of 1 atmosphere.

Table 3. Experimental activation energies from studies of evaporation, drying, moisture movement, and transpiration.

Experiment	Activation energy (kcal mole^{-1})	Symbol	Temperature range (°C)	Relative humidity (%)	Reference	Remarks
Evaporation of liquid water from outdoor tanks	11.5-15.0	E^*_{evap}	12.3-30.7	---	Sleight (1917)	Based on avg. temp. of water surface; 13 week-long expts.
Transpiration of excised leaves in potometers	22.1	E^*_{transp}	4.5-18.1	51-69	Kuiper and Bierhuizen (1959)	Data unaffected by variable light intensity; at 32.5° C and 25% R.H. transpiration lower than predicted.
Transpiration of *Ambrosia trifida* and *Helianthus annuus*	10.4-11.1	E^*_{transp}	21-49	20-80	Martin (1943)	Humidity affected rate but not temp. dependence; 7 expts. in darkness.
Evaporation from leaf-shaped blotting paper	6.8 5.9 5.1	E^*_{evap}	27-49	20 50 80		Based on air temperature. Evaporation into calm air.
Drying of water-sat'd. wood (Sitka spruce)	6.1	E^*_{drying}	25-80	50	Bateman *et al.* (1939)	Relative humidity 50% at all temperatures.
Drying of saturated clay	7.1	E^*_{drying}	27.8-43.3	10-45	Sherwood and Comings (1933)	Based on constant rate period.

Drying of sands	4.5 4.8 4.7	E^*_{drying}	55–76	—	Ceaglske and Hougen (1937)	Coarse, medium, and fine sand, respectively. Constant rate period.
	4.5 5.1 4.8		55–76			Coarse, medium, and fine sand, respectively. Falling rate period.
Drying of soil in cans floated on temp. bath[a]	16.1 7.0	E^*_{drying}	20–40 50–90	—	Harris and Robinson (1916)	Millville silt loam soil
	16.7 9.1		20–40 60–90	—		Coarse sand
Water flow in silicate mineral, heulandite[b]	5.4 9.1	$E^*_{unsat'd\ flow}$	20–75	—	Tiselius (after Barrer, 1951)	Flow normal to 201 and 001 faces of crystal, respectively.
Diffusion coefficient for water flow into soil[b]	1.0–5.0	E^*_{infil}	10–40	—	Biggar and Taylor (1960)	Millville silt loam
Weighted mean diffusivity for water flow into soil	3.5 3.6 3.0 2.0 4.0	E^*_{infil}	5–45	—	Gardner (1959c)	Pachappa sandy loam Yolo loam Indio loam Chino clay Traver sandy loam

[a]Range of temperature was 20 to 90° C, but plots of the data change slope in middle of the temperature range and there is a big difference in the activation energies of the different slopes.

[b]Only these workers reported activation energies; in all other cases the activation energies were calculated from reported data.

Psychrometric Aspects

The necessity for considering evaporative cooling and heat transfer in the drying of soil can be established by the following generalizations suggested by work on propagation of temperature in textiles (Cassie, 1940; King and Cassie, 1940; Cassie and Baxter, 1940; Crank, 1956, chpt. 13). By analogy with the systems of the above studies, it is apparent that (i) for a true equilibrium to exist between the drying soil and the environment, both the water vapor concentration and the temperature of the system must be in equilibrium with the hygroscopic soil, (ii) the immediate reaction of a mass of soil exposed to a new atmosphere is to attempt to bring that atmosphere into equilibrium with itself, and (iii) the latent heat of evaporation of water is large compared with the heat capacity of soil. (At room temperature the latent heat of vaporization of water is approximately 580 cal gm^{-1}, whereas the specific heat capacity of soil is about 0.2 cal gm^{-1} $^{o}C^{-1}$.)

If air with a lower vapor concentration, but the same temperature as the sample is introduced the sample immediately cools. The reason for this is that the quickest way for the sample to approach equilibrium with the new conditions is through a shift in temperature; this can be accomplished by a very slight loss in moisture content. If flow of the air which is now warm relative to the sample continues the sample will continue to lose moisture and will eventually come to a moisture condition in equilibrium with atmospheric drying conditions. Thus an essential feature of the moisture and temperature changes occurring in the drying of porous materials is confronted, namely, the existence of two modes of approach to equilibrium. These are a quick reaction involving a drop in

the temperature of the evaporating surface but an inappreciable change in moisture content, and a slow reaction involving a change in moisture content. The temperature change is propagated through the sample. It gives rise to heat flow within the sample and between the sample and the surroundings.

Whereas mass flow is amenable to treatment by reaction rate theory, the flow of energy (heat) appears not to have been so treated. Thus we seek different approaches for considering the rate limiting aspects of heat flow. These include:

(1) Utilization of an over-all heat transfer coefficient (Sherwood, 1929b; Gilliland, 1938, Chu, 1950) to help establish if and when thermal flow properties of the experimental system change. The heat transfer coefficient U for transfer of heat between the air stream and the soil is defined by

$$\frac{\Delta Q}{A\ \Delta t} = U\ \frac{T_2 - T_1}{x_2 - x_1} \qquad (60)$$

wherein $\frac{\Delta Q}{\Delta t}$ is the heat flux, $(T_2 - T_1)/(x_2 - x_1)$ is the temperature gradient between two points of interest, here the soil surface and some depth in the sample, and A is the cross-sectional area of the sample. As an approximation the heat flux can be obtained as the product of the evaporation rate times the latent heat of vaporization of pure water at the mean temperature of the depth interval. This analytical device is based on the hypothesis that as long as the heat transfer coefficient remains constant the thermal characteristics of the soil are having a uniform effect on the rate of evaporation. A decrease in U results when the heat flux decreases for a given temperature gradient. Such behavior might be interpreted as indicating that either evaporation is occurring at points deeper within the sample than while U was constant or that

there has been a change in the thermal properties of the soil system. The method is not without objection, but used in conjunction with a careful comparison between temperature distribution-time curves and drying-time curves it might help to establish how heat transfer affects the rate of evaporation.

(2) Calculations based on the thermal properties of soil. Richards et al., (1952, pp. 319f) present a tabular summary of heat capacity, thermal conductivity, and thermal diffusivity values for a large number of soils varying in texture, density, and moisture content. These values provide missing data which combined with information on the temperature and moisture distributions associated with a given evaporation rate might enable a comparison of the heat flux obtained in the experimental system with that necessary to maintain a given rate of evaporation. Such calculations can serve as a guide to the identification of conditions for which thermal properties of the soil could limit the energy supply to the sites of evaporation. The calculations are straight forward for a simple linear system, but become increasingly difficult for more complicated systems.

Flow Sheet of Analysis

It seems evident that the conclusions which will be reached in this study depend considerably upon how the moisture flow (as given by the evaporation rate), the moisture distribution in the test material, and the thermal effects interact during the experiments. Therefore, possible conclusions based on hypothetical behavior were outlined. The results are expressed in the flow sheet of Table 4. To use Table 4, the same number is followed through the first three columns on the left. The specific effects accompanying the number build up a case of evidence which suggests the conclusion listed in the right hand column.

Although the information of Table 4 is based on general considerations, it illustrates how widely the conclusions can vary depending upon experimental behavior. When it is recalled that, hypothetically, these divergent conclusions are all for the same sample, one realizes that caution must be exercised in interpreting the results. It is hoped that most of the hypothetically possible behaviors will not occur and that the numerical data will help to narrow the remaining possibilities to a manageable few.

Table 4. Flow sheet of data analysis. (Use of the flow chart: Reasoning along a path of observed temperature effect, moisture distribution, and evaporation rate as indicated by the numbers in parentheses below the specific effects leads to the conclusions in the right hand column. The conclusions correspond to the different cases built up.)

Temperature effect (at evaporating surface and in the sample)	Moisture distribution	Evaporation rate	Evidence is that:
Temp. decreases initially toward the wet-bulb temperature, then:	Changes for a while then approaches a steady state (3)		(1) Evaporation is governed more by heat flow than by moisture flow.
a. Stays low (1, 4, 5, 6)		Is constant for a while then decreases with time (4, 8, 10)	(2) Evaporation conditions change during the experiment; moisture flow is of a diffusion type.
b. Stays low for a while before climbing back toward the temperature of the air passing over the sample (2, 3)	Changes continuously during experiment, but: a. Is parabolic with distance from evaporating surface (1, 2, 4, 7, 8, 9, 10) b. Is linear with distance from evaporating surface	Decreases continuously from beginning of experiment (2, 7, 9)	(3) Evaporation rate will be low; evaporation rate is governed by moisture distribution.
Heat transfer coefficient:			(4) Initial rate of evaporation is limited by drying conditions, but by moisture flow later.
a. Remains constant over entire period of experiment (8)			(5) Heat conductivity of medium is poor; vapor phase moisture transfer is appreciable.
b. Remains constant for a while then changes to a lower value (7)	Water accumulates at evaporating surface (cool end) (5)	Reaches a steady value (1, 3, 5, 6)	(6) Temperature effect is dominant over moisture flow.
			(7) Heat transfer between circulating air and the soil is not limiting; moisture flow is limiting.
			(8) Heat and moisture flow interact.
Energy of activation is:	Water accumulates at end of sample away from evaporating surface (warm end) (6)		(9) The evaporation process is not limited by the energy sink of the phase transition per se.
a. $<\Delta H_{vap}$ water (9)			(10) The energy barrier to vaporization may be an appreciable factor in producing the observed evaporation rate.
b. $>\Delta H_{vap}$ water (10)			

METHODS AND PROCEDURES

General Description

Millville silt loam was packed homogeneously into lucite cylinders. Tensiometers were spaced logarithmically along the soil columns and calibrated thermistors were inserted into the sample through the lucite walls of the cylinder containing the soil. The entire soil column and attachments were immersed in a constant temperature bath. Air which had been passed through silica gel to bring its relative humidity to a constant low level was passed over one end of the sample at a given rate as controlled by a pressure regulator and flow meter. The moisture evaporated from the sample was trapped in a second silica gel column. The dry air entered the lucite tube containing the soil column at a point just above the soil surface and left through an opening diametrically opposite the point of entry. The other end of the soil column was in contact with a water reservoir through a porous disc (series A). The water in the reservoir was kept under the desired vacuum pump suction in order to maintain a constant moisture potential at one end of the sample. (In the runs designated as series B the sample was shorter and water was not replenished at the end away from the evaporating surface.)

In order to study the temperature dependence of the process the temperature of the bath was regulated at specific temperatures within the range 12.7 to 37.7° C for the various runs. The air passing over the sample was brought to the temperature of the bath by passing it through coils of copper tubing immersed in the constant temperature bath immediately prior to its passage over the soil column.

The data obtained at each reading included: (a) the temperature distribution in the soil column as obtained from the thermistor readings, (b) the cumulative evaporation, and the rate of evaporation from the periodic determination of the increase in weight of alternated silica gel columns used to trap the water evaporated from the soil column, and (c) the moisture distribution in the soil column as indicated by the tensiometer readings made at the same intervals of time that the other readings were made. These data enable one to study the relationship between the change in evaporation rate in a given time interval and the change in distribution of moisture in the same time interval. The data also enable one to compare the evaporative cooling effect with the evaporation rate at a given time.

A schematic drawing of the apparatus used in making the measurements is shown in Figure 1. The various parts and their operation are dealt with in more detail below.

Details of Apparatus and Measurements

Tensiometers

Number 762 Coors filter cones of porosity 5 were used for the porous cups of the tensiometers. These filter cones are ceramic cylinders about 1 cm in diameter and 5.5 cm long. The upper 2 cm of the open end is glazed leaving a porous wall surface area for contact with soil of approximately 2.5 cm^2. Cones of reasonably uniform conductivity were selected by applying a constant vacuum pump suction to burets attached to cones submerged in free water and measuring the rate of absorption. For one group of 23 cones the average conductivities for 7.6, 25.3 and 50.6 cm Hg suction were 1.4, 4.5, and 7.2 ml hr^{-1}, respectively.

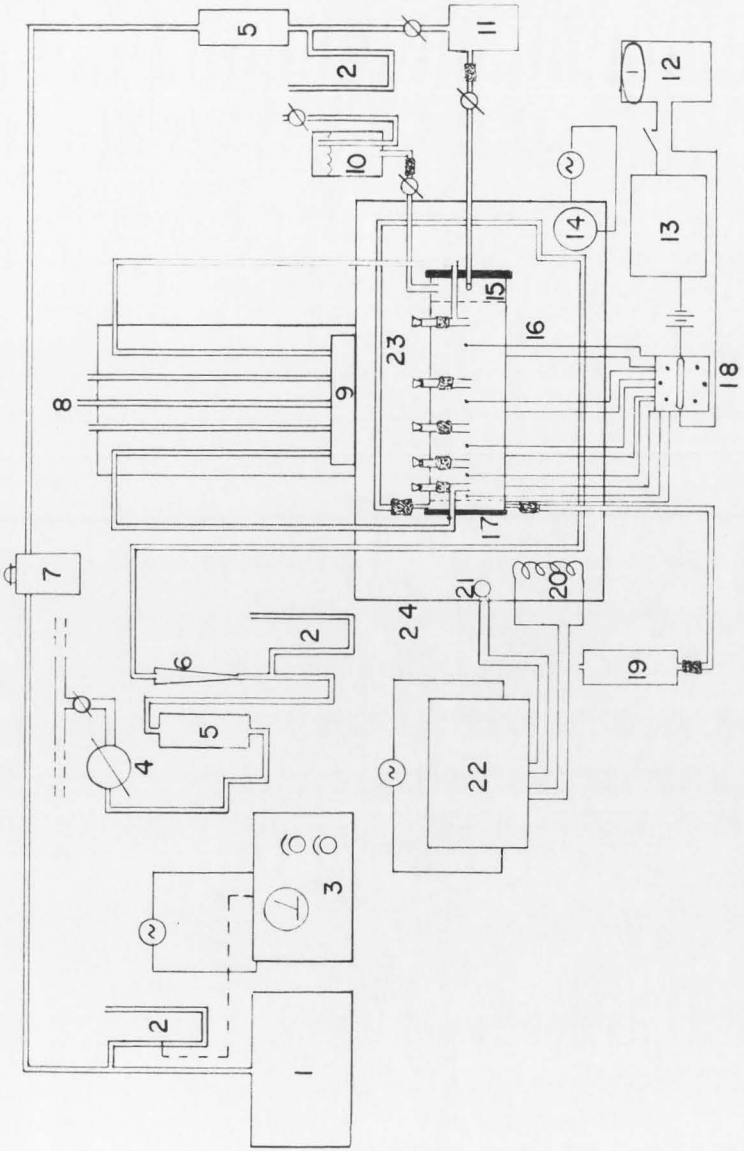
The cones were attached to a 1-1/2 inch long, 3/8 inch diameter copper tubing manifold. A short piece of glass tubing about the same diameter as the manifold was attached to the upper end of the latter to serve as an air trap during operation. A 3/16 inch copper tubing sidearm connected the manifold with the upper end of glass tubing immersed in a trough of mercury.

The porous cones of the tensiometers were imbedded in the soil within the lucite cylinders by inserting them through holes bored through the cylinder walls. The tensiometers were spaced at positions 2, 4, 8, 12, 16, 24, and 30 cm from the drying end of the 31 cm long soil columns (series A apparatus) and at 2, 4, 8, 12, and 16 cm from the drying surface in the 18 cm long soil columns (series B apparatus).

Because of the threat of leakage of water into the soil column from the water bath in which it was immersed, pieces of 1-inch thick lucite were filed and lathed so that a concave surface which matched the curvature

Figure 1. Apparatus of temperature dependence of drying experiments.

1 vacuum pump
2 mercury manometer
3 thermocap relay
4 flow regulator
5 air drying column
6 flow meter
7 manostat
8 glass capillaries of tensiometers
9 trough of mercury
10 water supply to reservoir
11 water trap from reservoir
12 galvanometer
13 resistance bridge
14 bath stirrer
15 water reservoir
16 thermistor leads
17 air gap at end of soil column
18 selector switch
19 silica gel absorber
20 bath heater
21 mercury thermoregulator
22 electronic relay
23 air temperature equalization coil
24 water bath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of the lucite cylinder was obtained. The lucite collar was then drilled through with a larger bit than had been used in making the openings in the cylinder walls. The holes of the lucite collars were positioned to surround the holes through the cylinder wall. The two pieces were then laminated together.

Molten canning wax (paraffin) was squirted into the opening between the tensiometer stem and the lucite wall. Even this precaution of increasing the depth of the wax seal failed to eliminate leakage on some occasions. In these cases the runs were terminated and new ones begun. Due to its low melting point, use of canning wax as a sealant was one factor in limiting the upper range of temperature used. The obvious disadvantages of such a sealant were tolerated in view of its virtues. These included the quick and easy disassembly of the apparatus when it was desired to make gravimetric moisture samplings or to re-determine the conductivities of the filter cones.

In operation the entire manometric system including the filter cone, the copper manifold, the air trap, the copper sidearm, and the glass tubing was filled then further flushed with hot, freshly boiled distilled water. On stoppering the air trap, the water in the porous cone quickly came to equilibrium with the soil water and registered the soil moisture suction by the position of the Hg-water interface in the glass capillary tubing. The tensiometers served satisfactorily in their range of operation--up to about 0.8 bars suction.

All the soil moisture potentials reported herein are corrected to the value at the porous cups according to the procedure of Richards (1949). This included subtracting the sum of the scale reading with the air trap

open plus the equivalent height from the air trap to the filter cone from the actual scale reading in operation. The lowering of the level of the Hg in the trough as Hg was drawn into the capillaries was ignored. The moisture suctions are reported in the same units in which they were measured (cm Hg) in the summarized data of the experiment given in Appendix I. They are generally reported in bars in the Figures in the text.

Thermistors

Temperature measurements within the sample were made with calibrated Western Electric model 17A thermistors. These thermistors are disc-shaped. The disc is 3/16 inch in diameter and less than 1 mm in thickness. The short leads furnished with the thermistors were extended by soldering about 80 cm lengths of ordinary lamp cord to them. The bare wires were then sprayed with clear liquid plastic. The thermistors were calibrated in the same constant temperature room using the same voltage supply, resistance bridge, and galvanometer as was used when the thermistors were imbedded in the soil column. The calibration operation entailed suspending the thermistors in continuously stirred water contained in a large Dewar flask. The water temperature was adjusted within the range of temperatures used in the experiments. The actual temperature of the water was estimated to hundredths of degrees on a thermometer graduated to tenths of degrees immediately after each thermistor calibration resistance reading was made. The thermistor-indicated temperatures reported are considered precise to only $\pm$ 0.1° C.

The calibrated thermistors were positioned in the center of the lucite column before soil was added. The procedure was as follows: Holes just larger than the lamp cord leads were drilled through the walls

of the lucite cylinders at points diametrically opposite each other along the lucite cylinders. (At least three different sets of spacings along the soil column were used. Since the data presented in Figures and more completely in Appendix I give the particular spacings for a given run they are not given here.) Because the thermistor beads were larger than the lamp cord leads--and hence also larger than the holes through the walls of the sample containing cylinder--the thermistor leads were threaded through the lucite tubing from the inside. "Armstrong's Adhesive A-1" (Armstrong Products Company, Argonne Road, Warsaw, Indiana) was applied over each exit hole and the cord at the point at which it emerged from the cylinder. On hardening, the A-1 adhesive was waterproof. It was brittle enough to chip off with a sharp tool, however, as was learned when it was desired to remove the soil sample from the cylinder for gravimetric determination of the moisture distribution in the soil column.

The thermistor readings were made manually. All the thermistor leads were attached to a multiple switch. Up to eight thermistors were employed in a given run. It was usually possible to adjust the potentiometer to the null point and record the bridge resistance for a given thermistor within a minute. This standard procedure of making thermistor readings at minute intervals was rigorously followed. The time at which the thermistors were read was recorded to the nearest minute. The official time was that of an ordinary electric laboratory clock with a "sweep" second hand.

Air preparation and flow

The air passed over the sample originated from the 50 pounds per

square inch air pressure line of the laboratory. It was "processed" by passing it successively through a flow regulator, a vertical glass column of 4.6 cm inside diameter which contained a depth of 30 cm of silica gel, then over 1 arm of a mercury manometer, through a G9145B "Predictability" flow meter (The Emil Geiner Co., 20-26 N. Moore Street, New York 13, New York), and finally through copper and rubber tubing coils immersed in the constant temperature bath. The air then passed over the soil surface and through a second silica gel column. The principle behind the use of the first and second silica gel columns is that when placed on opposite sides of the moisture source, the gain in weight of the second one will serve as an accurate measure of the moisture evaporated from the soil since the air leaving it will be reduced to the same moisture level as that which left the first drying column. The silica gel columns referred to (parts numbered 5 and 19 in Figure 1, p. 114) were both at room temperature and the silica gel in them was prepared in the same way. The silica gel of both columns was always changed while there was still a large amount of unmoistened gel in each. In early experiments two silica gel columns, one on top of the other, were often used to trap the moisture evaporated from the soil. The second one never gained weight until the one below it was practically completely moistened. The evidence is therefore good that the relative humidity of the air leaving both the air drying and the vapor trapping silica gel columns was the same.

The strong dependence of vapor pressure on temperature raised the question of whether the relative humidity of the air passing over the soil could have varied significantly as a function of the bath temper-

ature to which it was brought just prior to passage over the soil column. A hair hygrometer in the dry air line registered a constant reading of 6 per cent relative humidity (an erroneous absolute value, but constant) under all conditions of drying. Dehler (1940) reported that silica gel may be used to dry air and other gases to dewpoints below -60° F. For these reasons it is believed that the relative humidity difference between soil and passing air varied within narrow limits over the temperature range of the experiments.

The silica gel used contained a moisture indicating dye. The silica was always replaced by gel regenerated by drying at 150° C (Dehler, 1940; Skelly, 1950) long before the color change had permeated the entire length of the column. Two evaporation indicating columns of gel 30 cm long and 5 cm inside diameter were alternated. They contained about 380 gm of gel. Weighings were made on a pan balance with a scale graduated to 0.05 gm. The weighings were interpolated to 0.01 gm, however. This was deemed legitimate in order to reduce errors in the cumulative total.

For all except one run the reading on the G9145B flow meter during operation was 10. For the one exceptional run (13A) the flow meter reading was 5.9. Based on International Critical Table data for the density and viscosity of dry air at 645 mm Hg pressure, and formulas furnished by the manufacturer of the flow meter the air flow rate for the reading of 10 on the meter scale would correspond to about 3.5 and 3.3 liters min^{-1} at 10 and 35° C, respectively. These flow rates are for standard conditions of 70° F and 1 atmosphere pressure. At 20° C the reading of 5.9 on the flow meter corresponds to a flow of about 1.7 liters min^{-1} for the standard conditions.

There were 27 feet of 1/4 inch copper tubing plus about 8 feet of 3/8 inch outside diameter rubber hose immersed in the constant temperature bath. The object of this length of tubing was to obtain thermal equilibrium between the air entering the sample chamber and the bath. When the flow meter read 10, the pressure drop across the arms of the mercury manometer in the air flow line was 2.8 cm Hg. By "breaking" the system at various points it was found that the pressure differential (flow resistance) arose almost entirely in the copper and rubber tubing temperature equalization coils. No pressure drop across the soil column was detectable.

The air that passed over the soil surface entered the sample chamber through 1/4 inch copper tubing extending through the cylinder wall. The point of entry was centered at 0.5 cm above the soil surface. The delivery tube ended flush with the inside wall of the lucite cylinder. The exhaust arrangement was the same as that of the delivery tube and was positioned diametrically opposite the point of entry.

Temperature control

All experiments were carried out in a constant temperature room. In addition the soil column and attachments were suspended in a constant temperature water bath of dimensions 76 x 38 x 38 cm. Temperature control was effected by a continuous cooling, intermittent heating arrangement. The water was stirred constantly. When the desired bath temperature was greater than the air temperature, cooling was by evaporation and heat dissipation to the surroundings. When a bath temperature below room temperature was desired the cooling coils of a continuously operating refrigeration unit were immersed in the water bath.

The water temperature was kept constant within about 0.01° C by intermittent heating. The electrical circuit included a mercury thermoregulator, a resistance heating coil immersed in the water bath, a powerstat, and an "Aminco" electronic relay (American Instrument Company, Silver Spring, Maryland). When the mercury in the thermoregulator fell below the electrical contact point the electronic relay was actuated.

Apparatus of series A runs

All experimental runs designated as series A runs were made on soil columns 31 cm long and 25.5 cm^2 cross section (5.7 cm diameter). The 5.7 cm diameter of these samples arises from insertion of 31 1-cm width lucite rings inside a longer 6.9 cm inside diameter lucite tube in the region occupied by the soil sample. The use of lucite spacers greatly facilitated moisture sampling because the lucite spacers formed an inner cylinder which could be removed from the solid outer one and the sample could be readily dissected by cutting through the sample between the spacers. The use of the additional inner cylinder increased the thickness of lucite between the soil and the water bath to 1/2 inch, however, since both pieces of lucite tubing had walls 1/4 inch thick.

The outer lucite cylinder was approximately 3 cm longer than the inner cylinder which held the soil sample. The upper end of the lucite cylinder was closed by inserting a lucite disc draped in a gasket of rubber sheeting. The inserted disc was parallel to the surface of the sample at a distance of 1 cm from it. During drying of the soil columns a stream of the drying air was passed through this 1 cm air gap at the end of the sample.

The end of the lucite tubing 31 cm from the soil surface was fas-

tened to a water reservoir. The water reservoir was made from lucite tubing of the same outside diameter as the soil container. One end of the water reservoir, the one in contact with the soil, was a grade M "porvic" membrane (Pritchett & Gold and E. P. S. Company Ltd., Dagenham Dock, Essex, England). This membrane has an average pore radius of 5 microns. The other end of the water reservoir was closed by recessing the lucite column into 1/2 inch sheet plastic. The membrane was supported by a perforated and striated lucite disc. The water reservoir was attached to the lucite soil sample cylinder by wires drawn taunt between paired screws on the water reservoir and soil cylinder. Three pairs of screws separated by about 120 degrees around the cylinder held the water reservoir securely to the soil sample container. To prevent leakage the screws and the junction between the water reservoir and the soil cylinder were covered with Armstrong's adhesive, type A-1. The soil column was prepared with the water reservoir attached. Experience indicated that contact between the soil and porvic membrane was satisfactory.

During the various runs arbitrarily chosen suctions less than 6 cm Hg were maintained on the water reservoir. A "Thermocap" relay (Niagara Electronics Laboratory, Andover, New York) (Taylor, 1955) actuated a vacuum pump for rough vacuum control. Fine control of the vacuum was obtained by means of a "Cartesian Manostat" style No. 8 (Emil Geiner Co., 20-26 N. Moore Street, New York 13, New York). The suction obtained was indicated by a mercury manometer. The vacuum was transmitted to the water reservoir through rubber tubing attached to plastic tubing extending vertically upward from the highest point of the reservoir.

In order to keep the reservoir full at all times water was fed into it from an inverted 500 ml erlenmeyer flask which served as a mariott bottle. Care was taken that the rate water was supplied to the reservoir exceeded the rate at which water moved into the sample from the reservoir. Regulation was by a screw clamp on the air entry arm of the mariott bottle. The excess water flowed out the suction connection at the top of the water reservoir and was retained in a 500 ml vacuum flask trap between the water reservoir and the manostat. A silica gel column which protected the manostat from moisture accumulation absorbed an amount of moisture which was negligible in comparison to the total flow.

The tensiometer and thermistor installations in the soil columns of both the series A runs (apparatus just described) and the series B runs (apparatus next described) were dealt with in detail in separate sections. These descriptions are not repeated here.

Apparatus of series B runs

The apparatus of the series B runs was relatively simpler than that of the series A runs. The 18 cm long samples were contained in 6.9 cm inside diameter, 1/4 inch wall thickness lucite tubing. Total length of the cylinders was 21 cm of which 3 cm was utilized in stoppering the ends and providing the 1 cm air gap through which the evaporation inducing dry air flowed. The ends were stoppered by inserting snug-fitting lucite discs draped with rubber sheeting. As an additional precaution against leakage of water into the sample, a piece of rubber sheeting was spread over each end of the column and wired tightly to the cylinder. One end of the column had to be left open until after the sample was prepared. Difficulty with leakage at the ends was never encountered.

Sample preparation

Millville silt loam soil which was taken from the field, dried in air, and passed through a 2 mm round hole sieve was the raw soil used for all experiments reported herein. (A Wasatch coarse sand was used in some preliminary studies before the experimental techniques were perfected. The results for the Wasatch sand and Millville silt loam were similar.) Preliminary tests showed that a bulk density of 1.2 to 1.4 gm cm^{-3} could be readily attained on packing air-dry soil into the columns. Since the average bulk density of the plow layer of this soil is about 1.4 gm cm^{-3} in the field it was decided to attempt to obtain about the same bulk density in the laboratory. All results reported herein are for a bulk density of 1.40 (dry weight basis) unless otherwise specified.

After the thermistors and tensiometers had been placed in the soil cylinder the soil was added to the cylinder. The mass of soil required to give a bulk density of 1.40 gm cm^{-3} was placed in the column by letting the soil flow by gravity from a large glass laboratory funnel. The funnel opening from which the soil dropped into the cylinder was about 1/4 inch in diameter. While the soil flowed into the lucite column, the column was rotated and the soil packed by tapping the column gently on the table top.

When the weighed amount of soil had been tamped into the alloted volume, two thicknesses of filter paper were placed on the top of the soil column and water from an inverted bottle was allowed to drain onto the filter papers at a rate equivalent to a slow drip. While the samples were being wetted, small plastic capillary tubes through the cylinder wall at points about 1/3 and 2/3 of the way down the column were left

open to facilitate the escape of entrapped air.

After the soil columns had been slowly wetted in the above manner to a moisture content between field capacity and saturation, the filter papers were removed from the soil surface. If the samples were too wet they would slack down into the air cavity when placed horizontally. If too dry, uniformity in moisture distribution took longer to achieve. The process of obtaining the desired uniform initial moisture content for starting a run could be hastened by attaching the water reservoir (series A runs) and the tensiometers (both series A and series B) to the vacuum line and applying the desired suction.

The final equilibration of moisture and temperature conditions in the soil columns was made after all the measuring devices were in operating condition.

Characteristics of Soil Used

The physical and chemical properties of Millville silt loam have been studied by numerous workers. Some of the results considered most pertinent to the present study are summarized. Richards (1928), Richards and Moore (1952), Taylor and Heuser (1953), Ashcroft and Taylor (1953), and Soane[4] are among those who have reported information on the moisture characteristics of Millville silt loam soil.

Ashcroft and Taylor (1953) found that the moisture retention curve could be represented by

$$\theta = a\,\tau^{-b} \tag{61}$$

wherein θ is the moisture content (gm gm^{-1}) on the dry-weight basis, τ is the soil moisture suction in atmospheres, and a and b are constants having the values 0.159 and 0.308, respectively. They also considered the equation to be applicable only to soil moisture suctions greater than 1 atmosphere. Calculations were extended into the less than 1 atmosphere range, however, and found by direct sampling of the drying columns of the present study to express the moisture content well down to 0.3 atmosphere suction.

Table 5, in which the soil moisture suction is expressed in various units, gives some moisture contents calculated from expression (61).

Soane applied a thermodynamic flow equation to pressure cell outflow data. He found that the mobility coefficient showed a "complex and unexplained variation with the relative activity of the soil water", but

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[4]Soane, B. D. 1958. An application of a thermodynamic flow equation to water movement in unsaturated soil. M. S. Thesis. Utah State University. Logan, Utah.

Table 5. The moisture content of Millville silt loam as a function of soil moisture potential according to the expression of Ashcroft and Taylor (1953).

Soil moisture suction[a]			Moisture potential	Moisture content, θ
(cm Hg)	(cm water)[b]	(atmos)	(ergs gm^{-1} 10^6)	(gm gm^{-1})
22.9	310	0.3	.304	0.231
30.6	413	0.4	.405	.211
38.2	517	0.5	.506	.197
45.8	620	0.6	.608	.185
53.5	723	0.7	.709	.178
61.0	826	0.8	.810	.170
68.7	930	0.9	.912	.164
76.4	1033	1.0	1.013	.159
	2066	2.0	2.026	.128
	3099	3.0	3.039	.113
	4132	4.0	4.052	.104
	5155	5.0	5.065	.097
	6188	6.0	6.078	.092
	7231	7.0	7.091	.087
	8264	8.0	8.104	.084
	9297	9.0	9.117	.081
	10,330	10.0	10.130	.077
	12,396	12.0	12.156	.074
	14,462	14.0	14.182	.070
	15,495	15.0	15.195	.069
	18,594	18.0	18.234	.065

[a]For some other units of expression, see Taylor (1958).

[b]The common logarithm of these values is known as the soil moisture pF.

he was unable to determine whether or not this could be accounted for by uncontrolled variables in the flow system. He found that a very sharp minimum occurs at about 0.4 bars in curves obtained by plotting the "mobility coefficient" versus the pressure applied on the membranes of the pressure cells. Richards and Moore (1952) remarked that Millville silt loam is distinctive as compared with other soils in that it exhibits a low rate of change of moisture conductivity with suction over part of the suction range.

Information obtained from the characterization of Millville silt

loam by the Soil Testing Laboratory on the Utah State University campus[5] indicates that the size distribution of the surface 6 inches of Millville silt loam is: sand, 29 per cent; silt, 57 per cent; clay, 16 per cent. In the same source it is reported that the cation exchange capacity is 13.9 me 100 gm^{-1} of soil, that the $CaCO_3$ equivalent is 43.6 per cent, and that the pH of the saturated paste is 7.9.

[5]Courtesy of Mr. J. P. Thorne, director. Reported in National Cooperative Soil Survey profile description leaflet No. 663, February 11, 1959.

Description of a Typical Run

The apparatus was considered ready for a run to begin when all the measuring equipment was in position and functioning properly, provided the soil moisture and temperature readings had held steady for a period of at least 12 hours. To begin a run the flow regulator was adjusted to give a flow meter reading of 10. The information recorded for a given set of readings included the day, the time of day, the bath and room temperature, the cm Hg suction on the water reservoir, the air flow rate, the readings of all tensiometers and thermistors, the weight gain of the silica gel column in which the moisture that evaporated was trapped, and the difference between the inflow to and the outflow from the water reservoir in contact with the sample (series A only).

In chronological order the steps followed in obtaining a set of readings were: (1) the silica gel to be used in the first time interval ahead was removed from the 150° C oven and placed on the laboratory air ventilator in a covered pan where it cooled; (2) the thermistor resistances were measured and the resistances and the time (to the nearest minute) at which they were obtained was recorded; (3) one silica gel column moisture trap was removed and replaced by the one with which it was alternated; the time was noted and recorded; (4) the tensiometers were read and the readings recorded; (5) the air flow rate, the bath and room temperatures, and the vacuum on the water reservoir were checked and their values recorded; (6) the silica gel column removed in step three above was poured into a special weighing dish, and its weight gain determined and recorded; all the silica gel of the column was then spread in shallow layers in pie tins and placed in the drying oven; (7) the now

cool silica gel was removed from the laboratory ventilator and the standard amount (by weight) was placed in the column which was emptied in step six (additional dry silica gel was kept handy as an auxiliary supply); (8) the newly prepared column of silica gel was taken to the room of the experiment and the operation of all devices again checked. About half an hour was required to make a complete set of readings.

At the beginning of a run the temperature at the measuring points in the soil columns was very transient. Therefore for about the first two hours of operation the thermistors were read almost continuously. In general, all readings were made more frequently at the beginning of the runs than toward the end. Complete sets of readings averaged about six for the first twelve hours of operation, about six for each twenty-four hour period for a few days thereafter, and finally only four (and sometimes only two) per twenty-four hours until the runs were terminated.

A given experimental run usually lasted about ten days. The arbitrariness in the duration of the runs results from the fact that the time required for a soil column the length of those used in these studies to come to complete equilibrium with the evaporation conditions, that is, for the evaporation rate to become zero, approaches infinity. Such a time is obviously impractical experimentally. Hence a run was considered complete when the evaporation rate had decreased to a nearly constant low level, and the tensiometers failed as indicators of the soil moisture condition in the sample. Some runs had to be terminated sooner due to mechanical failure of apparatus or due to leakage of water into the sample from the water bath.

RESULTS

The objective of the present study was to gain evidence on the rate limiting process in the evaporation of moisture from soil by studying (a) the temperature dependence of the process, (b) the rate of evaporation as a function of moisture distribution in the soil, and (c) the temperature distribution resulting from evaporative cooling in relation to the rate of evaporation. In considering the results the thermal relations are presented first, the soil moisture relations second, and the rate theory (temperature dependence) last. From time to time it is necessary to bring in information not directly a part of any of the above main aspects of the study, however.

General Survey

A general survey of the experimental conditions associated with the various runs is given in Table 6. The complete data for all these runs are presented in summarized form in Appendix I. The data fall naturally into three groups. The series B runs form one group. They are distinguished from the series A runs by the facts that the soil columns were shorter (18 cm as compared with 31 cm), but larger in cross-sectional area (37.4 cm^2 in cross-section as compared with 25.5 cm^2) than the soil columns of the series A runs, and in that they were not in contact with water through a porous membrane at the end away from the evaporating surface as were the series A columns. Runs 5A and 6A form the second group. The remainder of the series A runs comprise the third group.

Table 6. A general summary of conditions of the various experimental runs in the drying of soil columns.

Series	Run	Bath temp.	Room temp.	Initial moisture suction	Duration of run	Cumulative evaporation	H_2O uptake from reservoir
		(°C)	(°C)	(cm Hg)	(hr)	(gm)	(ml)
A	5[a]	24.9	24	1.2	195	296	-36
	6[a]	34.9	35	3.1	165	235	-92
	4	24.9	24	4.4	427	628	~500
	9	29.1	30	4.6	454	396	409
	11[b]	22.3	22	4.2	101	147	74
	13[bc]	22.3	21	3.2	267	227	182
	14[b]	37.7	21	2.3	163	262	160
	16[b]	12.7	21	1.0	109	119	63
B	3	24.9	24	1.0	200	230	
	5	34.9	35	0.4	178	231	
	6	34.9	36	4.0	48	144	
	7	37.7	21	0.5	117	269	
	8	12.7	21	0.4	319	255	

[a]Considered different from other series A runs as explained in text.
[b]The same soil column was used for all these runs. It was rewetted between runs by standing the column upright and letting water flow dropwise onto two thicknesses of filter paper lying on the soil surface.
[c]Rate of air flow was 1/2 that of all other runs.

Runs 5A and 6A differ from the other series A runs in that water evidently reached the soil column via a leak at the tensiometer 12 cm from the drying end after a suction of about 10 cm Hg developed in the soil column at this point. The data are retained, however, because the only apparent effect of the water leakage into the sample was the shortening of the length of the drying soil column from 31 to 12 cm. Data shown later illustrate that these shortened soil columns behaved identically like the longer ones with respect to evaporation rate and time dependence of evaporation.

Temperature Effects

As shown in Table 6, the water bath in which the soil column and attachments were immersed was regulated at specific temperatures in the interval 12.7 to 37.7° C. The temperature distribution in the soil column of both the series A and the series B runs is shown in Figures 2 and 3, respectively, for the above mentioned temperature extremes. The data of Figures 2 and 3 well represent the range of temperature behavior exhibited by the soil columns as drying proceeded. At all bath temperatures the surface temperature dropped extremely fast as soon as air flow commenced. The temperature drop lessened with distance in the sample. At 5.0 cm from the evaporating surface it was never greater than 3° C although it was as large as 9.9° C (run 6A) at the 0.5 cm depth. The distance -0.5 cm in Figure 3 designates the temperature measurement at the midplane of the 1 cm air gap at the end of the sample through which the dry air flowed.

Temperature-time curves

When the data of the 11 runs in which the temperature distributions were measured, were plotted on the same scale and studied, certain general relationships were observed. In 8 of the runs the temperature of the soil columns began to climb back to the equilibrium temperature after a certain period of time had elapsed. The higher the bath temperature the faster the climb back to the equilibrium value,[1] and the sooner the return began. The exact time of the beginning of the return to the equilibrium temperature is difficult to identify. The lower the bath temperature, the more difficult it was to distinguish the low rate of climb from a

[1]The bath temperature is by definition the equilibrium temperature.

steady state distribution. Some runs, for example, 8B as shown in the lower part of Figure 3, exhibited periods of steady state behavior between temperature shifts. The various runs are not referred to as steady state temperature runs unless the same temperature pattern persisted for the major part of the duration of the run. Runs 4A, 5A, and 13A meet this criterion. Based on temperature behavior at the 0.5 cm depth, these runs exhibited steady state temperature distribution after about 10, 30, and 35 hours, respectively, which lasted for the duration of the runs.

The fact that in every case and at all times during the runs the lowest temperatures were always found to exist at the shallowest depth of measurement is good evidence that most of the evaporation occurred at sites near the surface of the soil column.

Evaporation rate-temperature depression curves

The relation between the rate of evaporation from the soil columns and the temperature depression at a given depth in the soil columns is shown in Figures 4 and 5. The temperatures are those at 0.5 cm from the evaporating surface of the soil column for the series A runs and at 1.0 cm from the evaporating surface for the series B runs. The temperatures were obtained from readings of calibrated thermistors. The rates of evaporation are in the units grams per hour per square centimeter of soil column cross-section. The evaporation rates reported are the ratio of the increase in mass of the silica gel in the moisture trap in a given time interval divided by the time interval.

The curves through the data of Figures 4 and 5 were fitted by eye. Every curve goes through a maximum. On the right side of the maxima the curves are linear. To the left of the maxima the curves are nonlinear but the data are not extensive.

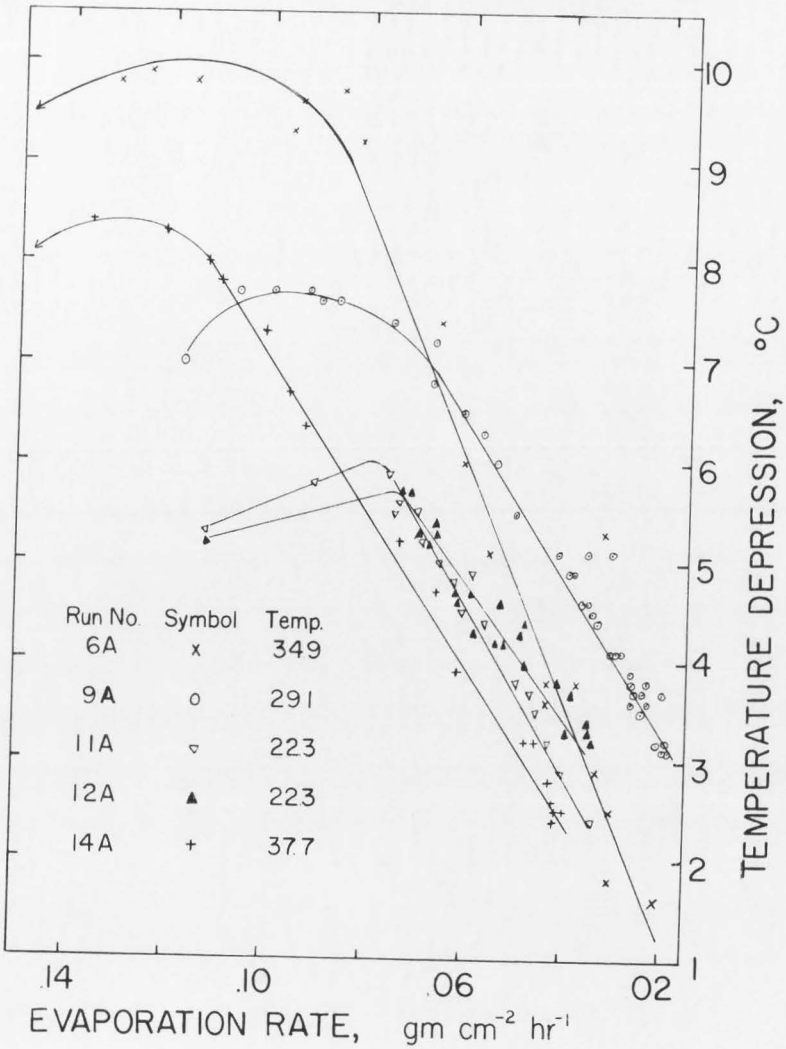

Figure 4. The relationship between the evaporative cooling at the 0.5 cm depth and the rate of evaporation for several series A runs.

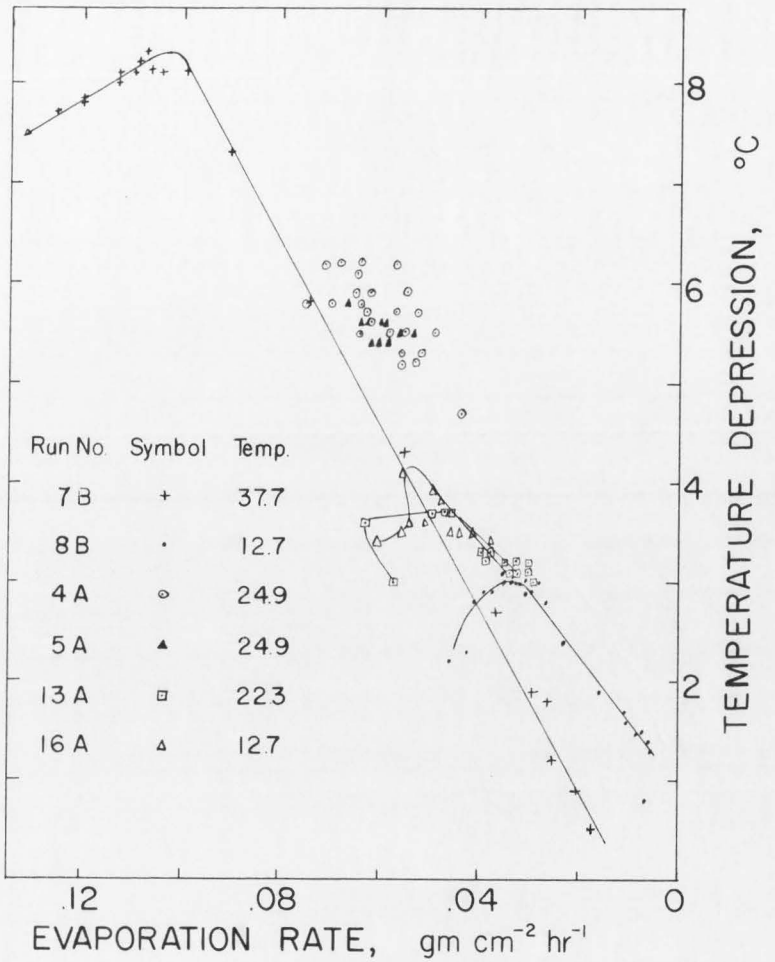

Figure 5. The relationship between the evaporative cooling and the rate of evaporation for two series B and three series A runs.

The beginning of the drying of the soil columns is represented by the left end of the curves. This time period of the experimental runs is considered first. The duration of the first time interval was usually 0.75 hours and the rate of evaporation was higher than at any time thereafter. One might expect the temperature wave from the surface to have penetrated to the 0.5 cm depth (series A runs) within 0.75 hours. However, for the nine series A runs reported, the average time required for the minimum temperature to be obtained at 0.5 cm from the soil surface was 4.4 hours. In no case was the elapsed time less than 2 hours. The explanation of the maxima in the evaporation rate-temperature depression curves is then that whereas the evaporation decreased continuously with time, two to four readings had been made before the temperature minimum was measured at the 0.5 cm depth. The necessary consequence is the maxima in the evaporation rate-temperature depression curves.

Thus the maxima in the curves of Figures 4 and 5 correspond to the region of the minima in the temperature-time curves of Figures 2 and 3. A temperature-time curve such as that of run 7B (shown in Figure 3) which possesses a broad minimum with many data points on it, possesses a maximum in the evaporation rate-temperature depression curve with about the same number of points on it. However, there is no correspondence between the shapes of the minima in the temperature-time curves and the maxima in the evaporation rate-temperature depression curves. That is, a broad (narrow) minimum in the temperature-time curves is not necessarily associated with a broad (narrow) maximum in the evaporation rate-temperature depression curves.

The vertical displacement of the maxima is a function of the equilibrium temperature. This is as expected from psychrometry theory which

predicts greater wet-bulb depressions the higher the dry-bulb temperature.

For some of the runs, particularly several in Figure 4, the maxima of the curves are very broad. This means that during the time of the runs corresponding to the data of the maxima, the temperature depression was nearly constant whereas the evaporation rate was decreasing. If the temperature depression during this time period had been a direct function of the evaporation rate there would be no maxima in the curves. On the other hand, if the temperature depression had governed the evaporation rate, the latter would not have decreased. It appears, therefore, that during this period neither the evaporation rate nor the temperature depression was a function of the other.

To the right of the maxima, the evaporation rate and the temperature depression regress linearly, that is, the rate of evaporation and the temperature depression are highly correlated. Furthermore, all the curves of Figures 4 and 5 have about the same slope in this region. Thus the rates of evaporation of the various runs are equal for equal temperature depression for all equilibrium temperatures in the range studied.

Figures 4 and 5 contain other information on the relation between temperature depression and evaporation rate. Runs 11A and 12A of Figure 4 differ from run 13A of Figure 5 only in the rate of flow of the dry air over the soil column. In run 13A the air flow rate was only one-half that of runs 11A and 12A (approximately 1.7 liters min^{-1} compared with about 3.4 liters min^{-1}). Runs 11A and 12A are duplicate runs to check the reproducibility of results. All three runs were conducted at a bath temperature of 22.3° C on the same soil column. The soil column was removed from the bath and rewetted between runs. At the maxima in the evaporation rate-temperature depression curves the results of the duplicate

runs are reproducible to within 0.3° C in temperature depression and 0.006 gm cm^{-2} hr^{-1} in the evaporation rate.

The evaporation rate and temperature depression at the maximum in the evaporation rate-temperature depression curve for run 13A are about 0.6 the value of the same quantity for runs 11A and 12A. This comparison of the effect of changed air flow rate on the evaporation behavior indicates that the initial rate of evaporation in these experiments was a function of the rate of flow of air.

In the cases of runs 4A and 5A a steady state temperature distribution was achieved which began immediately following the rapid initial temperature depression. As required by a high correlation between temperature depression and rate of evaporation the data points for these runs are closely bunched (see Figure 5)[2]. The fact that the temperature depression and the rate of evaporation are highly correlated in both the steady state and transient state evaporation runs raises an interesting question. The question is, does the evaporation rate control the temperature depression or the temperature depression control the rate of evaporation? In other words, which is the independent and which the dependent variable? We consider the question by arguing as follows:

On the macroscopic scale the endothermic nature of the phase transition suggests that for a given set of thermal characteristics of the system the temperature depression should be proportional to the rate of evaporation. However, as evaporation continues the soil dries and the thermal properties of the soil undoubtedly change. Thus one would not

[2]Many more data pairs than are seen in the figure are available for these runs, but since the temperatures were steady state, the plotted points often fall upon each other and cannot be shown in the figure. This is particularly true of run 5A.

necessarily expect a linear relation between evaporation rate and temperature depression over the whole range of soil moisture condition from near saturation to equilbrium dryness, unless the thermal properties of the soil change by an amount inconsequential in influencing the relation.

Figure 6 aids in understanding the thermal behavior of the system of this study. One of the curves of this Figure depicts the temperature drop at the 0.5 cm depth in the soil column at the beginning of the run. The other curve shows the time dependence of the return of the temperature to the equilibrium temperature when the run was terminated. To obtain the latter data the soil column was left sitting in the bath after the air flow was stopped and the thermistor readings were made in the usual manner. This column had been drying for 195 hours, and the tensiometer at the 2 cm depth was no longer operative.

The curves of Figure 6 indicate that the thermal conductivity of the moist soil and the dry soil do not differ radically. These data together with the findings on the time required for the temperature minimum to be reached at the 0.5 cm depth in the soil columns indicate that the thermal conduction of the soil is poor. Such behavior is consistent with a temperature depression which is governed by the rate of evaporation. That the evaporation rate did determine the temperature depression is supported by many isolated instances in the data in which rather sharp temperature changes at the shallow measuring depths paralleled changes in the rate of evaporation.

In summary, the analysis of the data presented in this section indicates that (i) the initial rate of evaporation in these experiments was governed by the rate of flow of air over the soil column, (ii) the thermal conductivity of the soil is low at all moisture contents, and

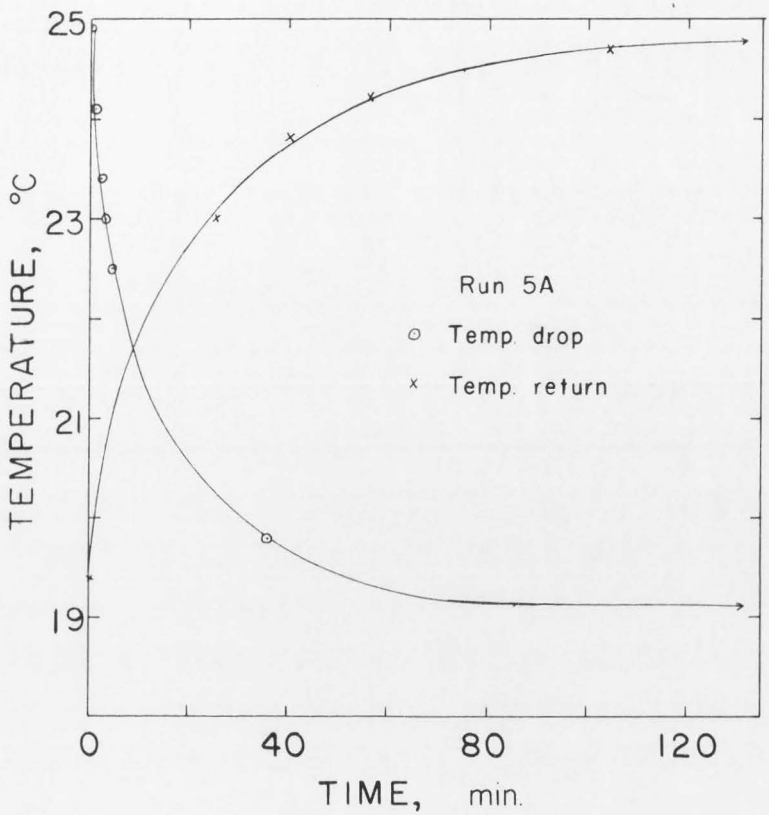

Figure 6. Details of the temperature fall at the beginning of run 5A and the return of the temperature to the equilibrium temperature when the run was terminated. (Temperatures are those at 0.5 cm depth in the soil column.)

(iii) no simple correlation between rate of evaporation and temperature depression exists until the temperature begins to climb back to the equilibrium value. The rate of evaporation then governs the temperature depression and a high linear correlation exists between the two.

Moisture Distribution

Moisture suction-distance curves

Figures 7 and 8 illustrate the relation found to exist between the soil moisture suction and distance from the evaporating surface at various times during runs 7B and 11A. The data show that the soil moisture suction is a linear function of the logarithm of distance from the evaporating surface. (The difference in extent of the abscissa in Figures 7 and 8 is due to the difference in length of soil columns. The series B soil columns were 18 cm in length, whereas the series A soil columns were 31 cm long.)

In comparing the two Figures, it may be noted that the slopes of the lines in Figure 8 are less than they are in Figure 7 for corresponding values of the soil suction at the 2 cm depth. This development of steeper suction gradients in the series A runs at lower suctions was a characteristic difference between the series A and series B runs. It seems to be a system difference which arose from differences in boundary conditions of flow including column cross-section and length, and moisture replenishment.

The fact that a measurable suction gradient developed within a few hours demonstrates that moisture adjustments occur quickly at all depths in response to moisture decrease at the surface.

Water flow from artificial water table

The suction behavior at the 25 and 30 cm depths in the series A runs, as exemplified by the results of run 11A in Figure 7, is of interest. In these runs there was a "porvic" membrane separating the soil column from the water reservoir. At the beginning of the run the water in the soil and in the reservoir were in equilibrium. However, when drying

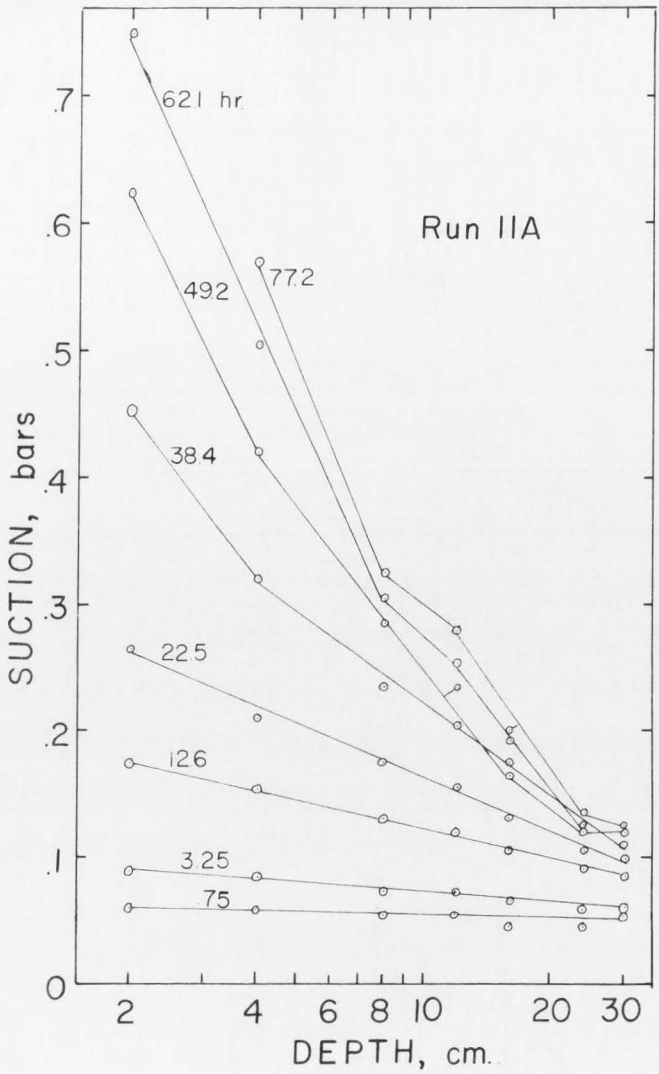

Figure 7. Soil moisture suction as a function of depth in the soil column with time as parameter. Run 11A.

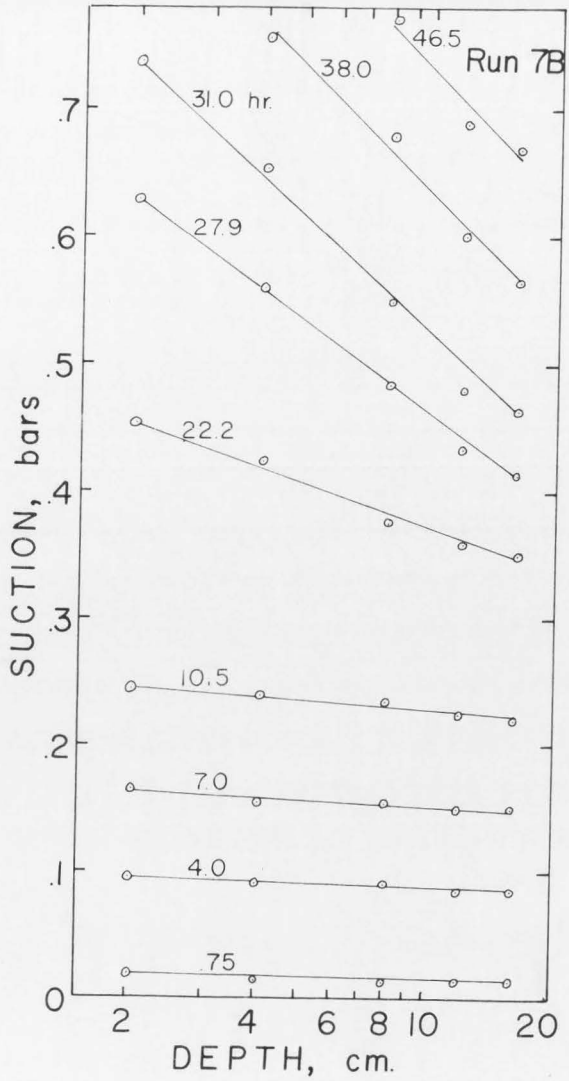

Figure 8. Soil moisture suction as a function of depth in the soil column with time as parameter. Run 7B.

began at the soil surface due to evaporative loss of moisture, the typical semi-logarithmic suction distribution developed. It was not long before the suction in the soil at the 30 cm depth was sufficient to induce water transfer to the soil column across the membrane. The interesting point is that for all series A runs the suction at the 30 cm depth rose to 9 to 10 cm Hg then held essentially constant. This indicates that the suction difference across the porvic membrane had to be of the order 3 to 5 cm Hg before the water replenishment from the reservoir kept pace with the evaporative loss of moisture from the soil surface.

One of the original reasons for using the artificial water table in the form of the water reservoir in contact with the soil at the end of the column distant from the drying surface was to maintain a constant water content at one end of the sample. A consequence of the above finding is that the constant moisture condition sought was not obtained at the beginning of the experiment but at a later time. This would complicate any attempt to consider the data of the entire runs by any treatment which depends upon the boundary condition of constant moisture content at one end of the sample.

Another anticipated use of the data of water transfer across the membrane at the end of the column was to determine if, when the evaporating end of the column dried and the rate of evaporation decreased, the soil column would partially rewet and if so to what extent. It was thought that tensiometer behavior would reflect this rewetting. The tensiometers near the soil surface became inoperative before rewetting at these depths could occur, however, and the operation of those in the middle distances was often questionable. (When the tensiometers approach

their limit of operation, their readings change very slowly and it is difficult to know exactly when they become inoperative.) The only conclusion reached in this respect was that the water from the reservoir never penetrated to within 12 cm of the soil surface as a rewetting front. In the case of run 4A the evidence is that water movement from the reservoir did affect the behavior of the tensiometer at 16 cm from the surface quite drastically. The rate of water transfer across the membrane from the reservoir to the soil did exceed the rate of evaporation of water from the soil column by the time the runs were terminated.

Moisture content-distance curve

The relation between the moisture content on the dry weight basis and the distance from the soil surface as determined by direct gravimetric sampling at the end of three series B runs is shown in Figure 9. It is seen that the moisture content changes very rapidly near the evaporating surface. In all three cases the rate of change of moisture content with distance is very gradual beyond 4 or 5 cm.

From the moisture distribution of Figure 9 it is evident that the rate of replenishment of water to the soil surface could not keep pace with the rate of evaporation. The separate contributions of liquid unsaturated flow and water vapor diffusion can not be assessed from the measurements made. As the surface layer became drier the relative contribution of vapor diffusion should have increased. If so, it did not offset the decrease in liquid flow since the rate of evaporation decreased with time.

The moisture distribution shown in Figure 9 is the parabolic moisture distribution referred to in the review of literature. It is the linear coordinate expression of the soil moisture suction distributions

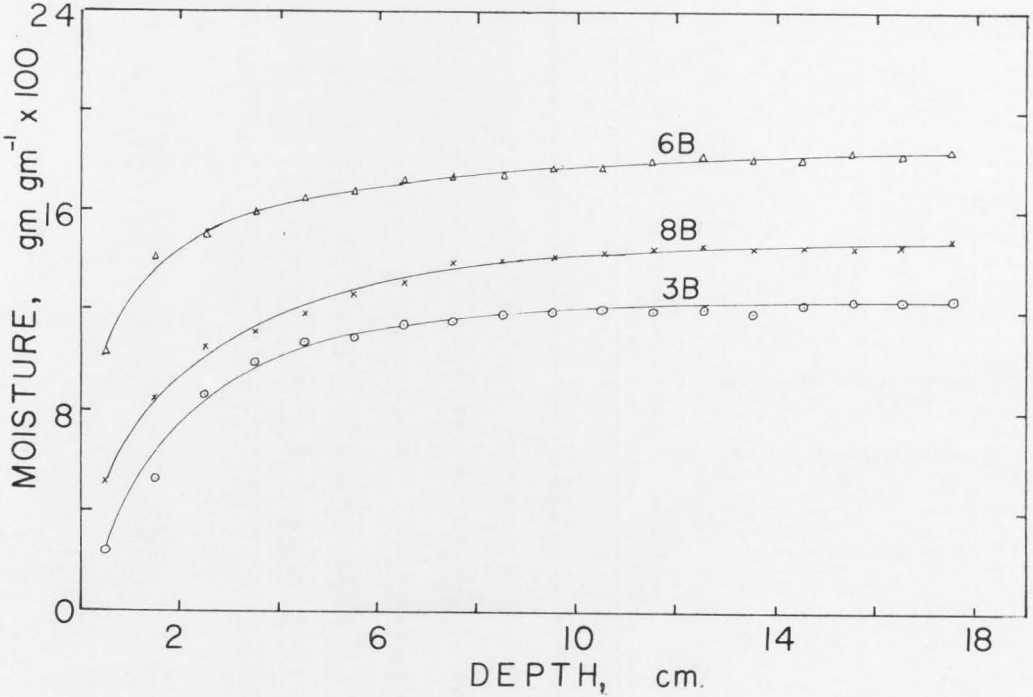

Figure 9. The moisture distribution in the soil column as determined by gravimetric sampling at the end of three runs of the B series.

of Figures 7 and 8. The discovery[3] or rediscovery of this characteristic moisture distribution in the drying of soil may be the most significant result of this study because of what it implies concerning boundary conditions for mathematical solutions of moisture flow, for the attention it focuses on moisture conditions close to the soil surface, and experimental requirements in terms of accuracy of measurement and the distribution of measuring devices with respect to the reaction interface. These implications will be considered more fully in the discussion of the results.

Moisture suction-time curves

The next result to be considered is also an interesting one. It is the log-log relation between suction and time shown in Figure 10. The number of slope changes causes one to doubt its generality. However, since it involves time and moisture suction, which on integrating over a depth interval yields a quantity directly related to the net flux of water out of that region in the given time interval, it hints at what to expect in moisture flow as a function of time.

The relative slopes of the plots of Figure 10 are directly the relative rates of change of suction with time. As shown in the family of five curves for the depths 2, 4, 8, 16, and 30 cm of run 11A the soil moisture suction changes at all depths but with a decreasing rate the greater the depth.

Moisture distribution-evaporation rate relationships

In attempting to establish whether or not the soil moisture distribution had a significant effect on the rate of evaporation independent of the temperature, the rate of evaporation was plotted against the soil

[3]After it was found experimentally in this study it was looked for in the literature.

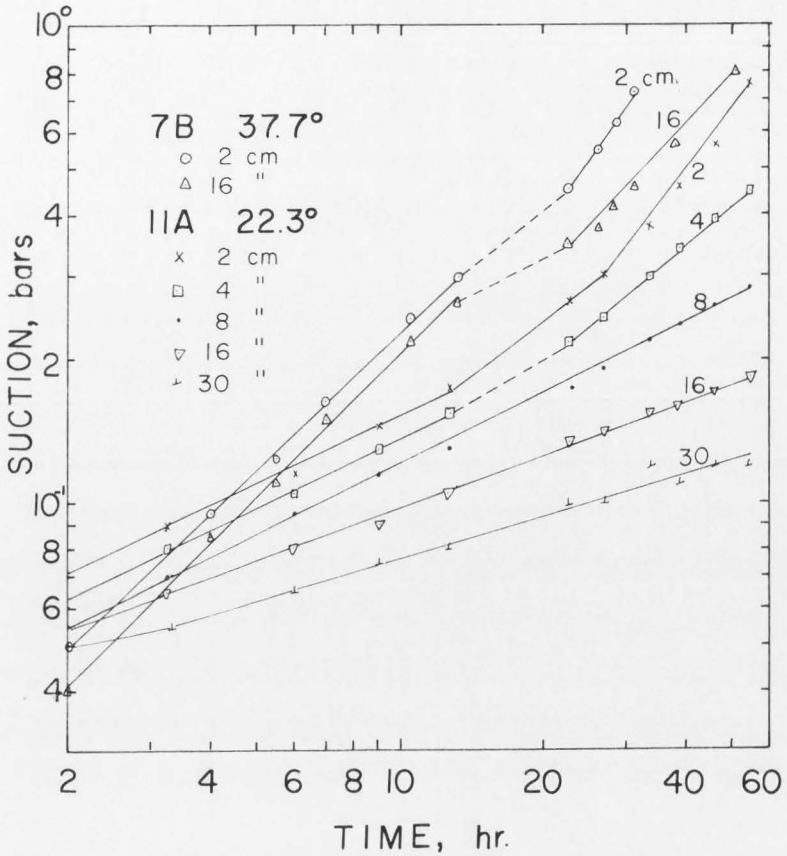

Figure 10. Soil moisture suction as a function of time since run began for runs 11A and 7B.

moisture suction at the 4 cm depth in the soil column of several runs of both the A and B series. Some of the results are shown in Figure 11. The arrows on the figure indicate the time at which the evaporation rate-temperature depression curves of Figures 4 and 5 become linear to the right side of the maxima.

For all runs there was a rapid initial decrease in the rate of evaporation with only a small change in the tensiometer reading. The curves then leveled off for a time before decreasing again. The sharp initial drop-off in rate of evaporation is probably not a function of the soil moisture condition.

Through the flattened range, the evaporation rate changed slowly compared with the change in moisture suction at the 4 cm depth as indicated by the tensiometers. The fact that the linear relationship between the rate of evaporation and temperature depression began, in most cases (see arrows on Figure 11), just as the flattening of the curves of Figure 11 was occurring cautions against interpreting the result in terms of temperature effects. If the capillary conductivity of Millville loam is nearly constant over a range of suction in the region of 0.4 bars (Soane)[4] and lower (Richards and Moore, 1952), this is a logical explanation for the slow rate of decrease in the rate of evaporation for the flat portion of the curves of Figure 11. The rapid drop-off in the rate of evaporation as the suction at the 4 cm depth approached the upper range of operation of the tensiometers is believed to be a real effect of moisture distribution on the rate of evaporation.

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[4]Soane, B. D. 1958. An application of a thermodynamic flow equation to water movement in unsaturated soil. M. S. Thesis. Utah State University. Logan, Utah.

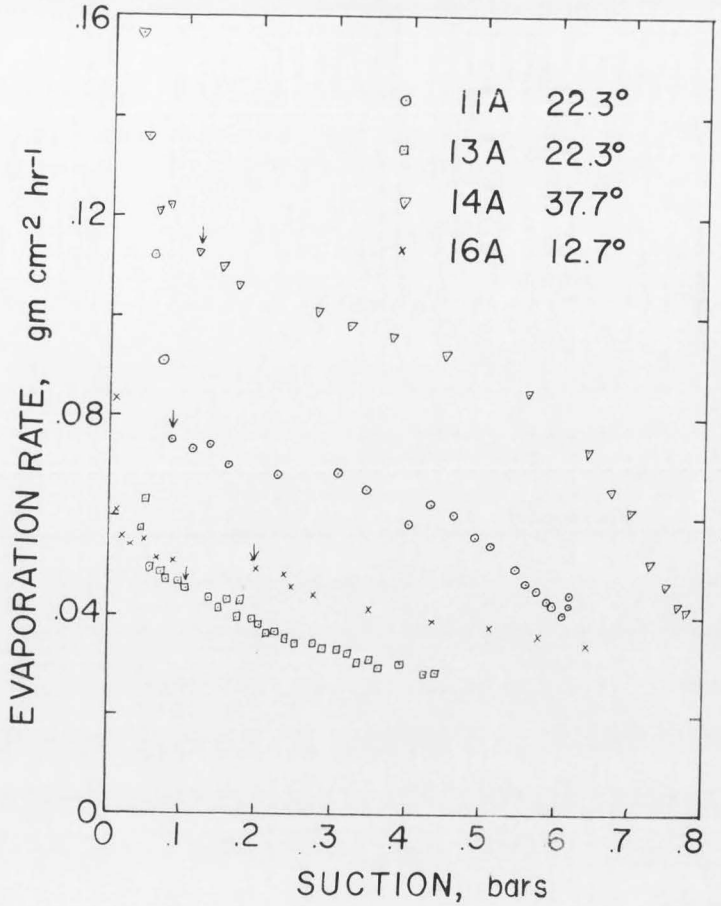

Figure 11. The relationship between the rate of evaporation and the soil moisture suction at the 4 cm depth for several series A runs. (The arrows indicate the time at which the evaporation rate-temperature depression curves of these runs, shown in Figures 4 and 5, become linear on the right side of the maxima.)

Evaporation-Time Relationships

The consideration of any rate process requires that the progress of the reaction be followed in time. In Figures 12 and 13 is shown the cumulative evaporation Q as a function of time t plotted according to

$$\log Q = \log a + b \log t. \qquad (25a)$$

In equation (25a) the parameter b is the slope of the lines in Figures 12 and 13, and a is the intercept on the ordinate at unit time, i.e., the evaporation at unit time. The slopes actually obtained in these experiments as determined from a least squares regression analysis are presented in Table 7. Table 7 also includes data on the time of occurrence of the slope change in those runs in which the slope changed during the course of the run, the number of data pairs in the statistical analysis, and the value of the evaporation rate at 1 hour as obtained from plots of the data extended to shorter time periods than are shown in Figures 12 and 13.

The initial slopes of the lines through the data are very nearly the same. This is reflected in the closeness to parallelism of the plots in Figures 12 and 13. Column 4 of Table 7 gives the numerical value of the slopes. The average for all runs is 0.910. A number of the plots change slope at times greater than 40 hours. The time at which the slope change occurs is generally greater the lower the equilibrium temperature of the runs. This suggests that the soil moisture condition associated with the change of slope may have been more nearly the same than was the time when the slope change occurred. The absence of a slope change is exhibited only by runs at temperatures of 24.9° C or lower; it appears likely that the moisture distribution associated with the slope change may never have been established in some of these runs.

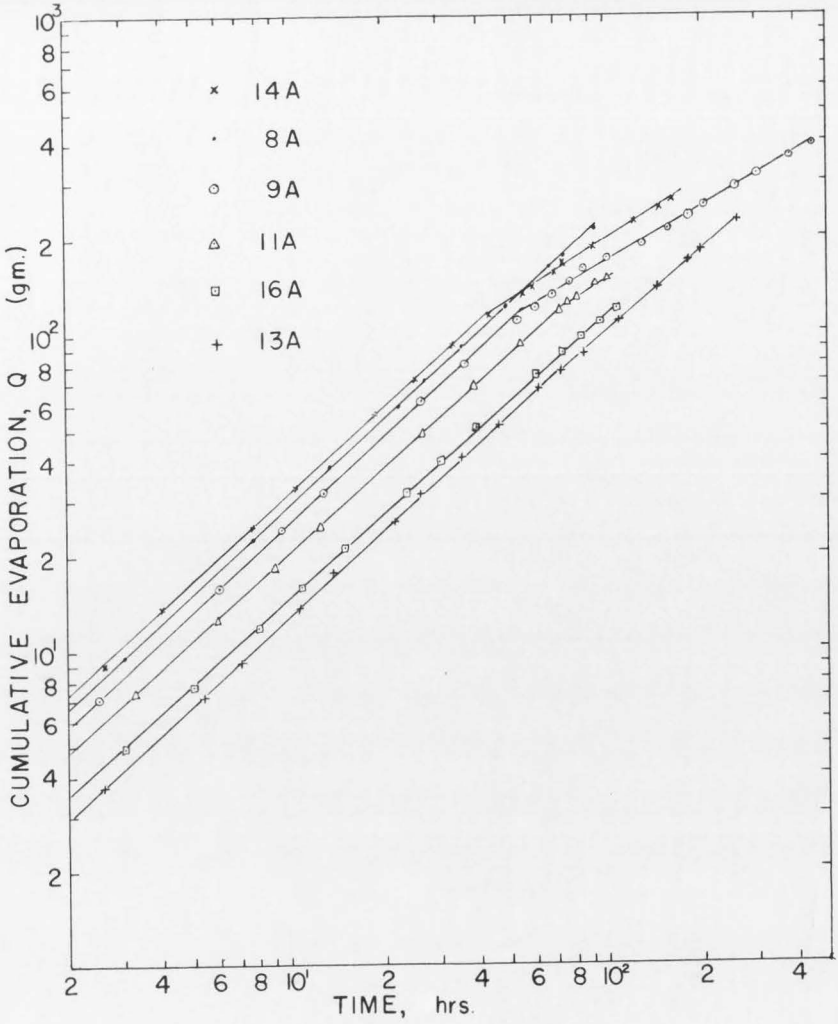

Figure 12. Cumulative evaporation as a function of time.

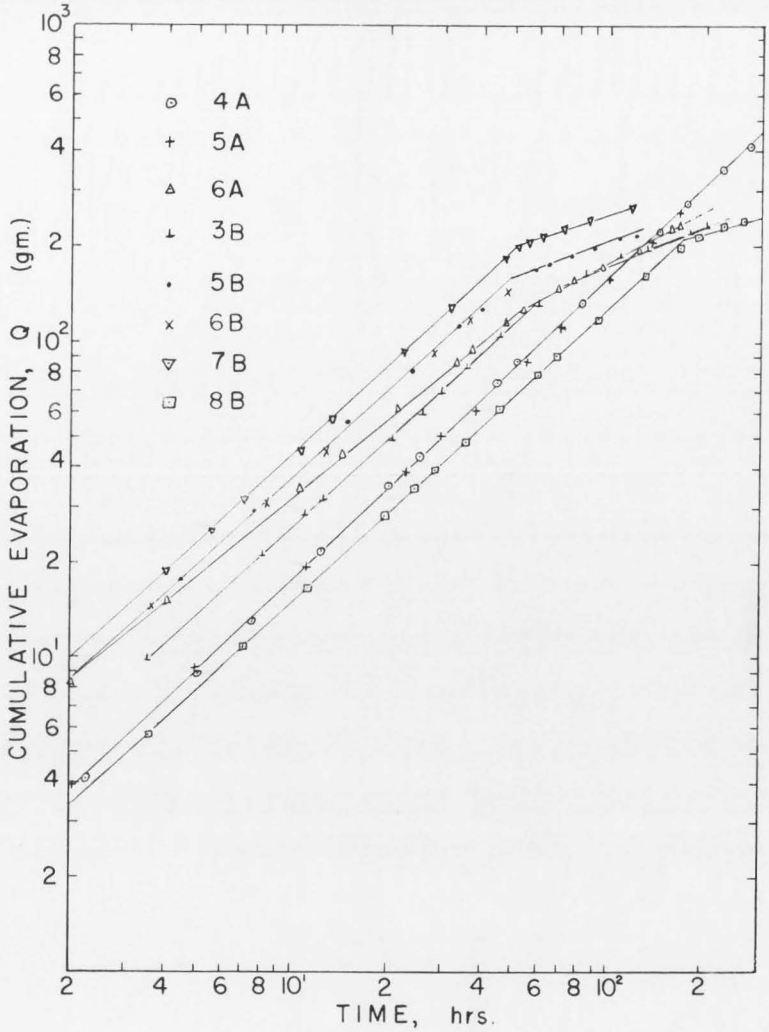

Figure 13. Cumulative evaporation as a function of time.

Table 7. The slopes b, the ordinate intercepts a, and the number of item pairs in the statistical treatment of the runs of Figures 12 and 13.

Run	Temperature (°C)	Intercept, a (graphical) (gm)	Initial slope, b	No. items, n	Time of slope change (hr)	Slope, b, after change	No. items, n
4A	24.9	1.89	0.955	52	None		
5A	24.9	1.05	.945	25	None		
6A	34.9	4.70*	.798	10	54	0.532	13
8A	34.9	3.50	.907	14	None		
9A	29.1	3.00	.913	9	55	.583	40
11A	22.3	2.75	.886	17	73	.679	6
13A	22.3	1.60	.895	50	None		
14A	37.7	3.80	.899	52	34	.622	17
16A	12.7	1.90	.918	16	None		
3B	24.9	3.10	.924	13	59	.428	17
5B	34.9	4.73	.924	8	55	.360	5
6B	34.9	4.75	.899	11	39	Insuff.data	
7B	37.7	5.23	.930	14	51	.360	8
8B	12.7	1.70*	.952	22	165	.311	12

*Poor agreement between extension of slope through unit time (1 hour) and experimental value at 0.75 hours.

The intercept of the cumulative evaporation-time curves on the ordinate is in the order of the equilibrium temperature. This is in agreement with the fact that the initial rates of evaporation were a function of the equilibrium temperature. This effect of temperature is operative at least to the time of the slope change. (In order that the plots be parallel the nature of logarithms requires that the difference between the cumulative evaporation expressed by successive lines increase on moving upward on the cumulative evaporation axis.) For example, if runs 9A and 11A of Figure 12 are considered, the difference in cumulative evaporation for the mentioned runs is: at 2 hours, 1 gm; at 10 hours, 5 gm; and at 40 hours, about 19 gm.

Whereas the cumulative evaporation was a function of the equilibrium temperature it was very insensitive to the temperature distributions

which were measured in the soil columns during the course of drying. This is evident from the observation that there is no inconsistency[5] in the cumulative evaporation results of Figures 12 and 13.

The reproducibility of the results is very important in such temperature dependence experiments, particularly since the length of time required to make a run limits the number of runs which can be made. The data of run pairs 4A and 5A, and 5B and 6B are seen in Figure 13 to be reproducible to the extent that only one line is drawn through the data for each pair. In both cases the runs are duplicates on the same sample under the same experimental conditions.

Nonreproducibility in the results, when the results are presented as in Figures 12 and 13, stems from differences in the initial rates of evaporation. This is because the evaporation during the first time interval of the runs--usually 0.75 hours in these experiments--controls the displacement on the ordinate. Of the runs reported in Table 7 the linearity of the plots extended down to 0.75 hours (hence through the intercept value, a) except for runs 6A and 7B. In these two cases the evaporation during the first interval was higher than predicted from the rest of the data. The intercepts reported for these two runs therefore differ considerably from those that would have been reported if guided only by the values at 0.75 hours. The results for run 12A are not reported in Figures 12 and 13 because the recorded evaporation for the first time interval is completely out of line with results for the other runs. At later time periods the measured evaporation rates for run 12A are in good

[5]It must be cautioned that a small, real effect might not be detectable because of the progressive insensitivity of logarithmic functions as time and cumulative evaporation increase.

agreement with those of run 11A (see Figure 4), with which 12A is a duplicate run.

As was noted in connection with Table 6, p. 132, there are considered to have been three different soil column lengths in these experiments: 31 cm, 18 cm, and 12 cm. The 12 cm soil columns (runs 5A and 6A) were not designed but "happened" due to leakage at the tensiometer at the 12 cm distance. Runs of the A series also differed from those of the B series in that they possessed the apparatus for maintaining an artificial water table; the B series columns were not so equipped. The results shown in Figures 12 and 13 fail to show any differences in the evaporation results which could be attributed to column length or water supply[6]. This result and the soil sampling information represented in Figure 9, p. 151, indicate that, in relation to moisture distribution, the evaporation behavior is dominated by the moisture distribution in the first few cm of soil depth.

The evidence obtained thus far eliminates the temperature distribution (but not the equilibrium temperature) as a significant influence on the cumulative evaporation. Apparently the thermal properties of the system had an essentially constant influence on the drying process at all equilibrium temperatures and moisture distributions.

The drying conditions external to the soil column (including the capacity of the air to take on moisture and the heat supplied by the passing air) and the moisture transfer within the sample are left as possible rate limiting processes in evaporation. If unsaturated flow of moisture were limiting the rate of evaporation the cumulative evapo-

[6] See footnote 5.

ration would be a function of the square root of time (Crank, 1956, p. 270). If, on the other hand, the initial evaporation rate was being limited by the external drying conditions the drying rate would be constant for a while, i.e., proportional to $t^{1.0}$.

Columns 4 and 7 of Table 7 contain the numerical values of interest for testing the above predictions. The average value of the exponent on time up to the time of the first slope change in Figures 12 and 13 is 0.910. After the slope change the average value of the exponent on time is 0.471. Thus the evidence is very good that up to the time of the slope change evaporation was limited by external drying conditions whereas after the slope change evaporation was limited by water transfer within the soil columns.

Rate Theory

The application of chemical kinetics to drying consists of (i) following the drying process as it proceeds with time at a given temperature, then expressing the results by a rate equation, (ii) repeating the experiments at a series of temperatures so that the temperature dependence of the drying rate can be obtained, and (iii) relating the temperature dependence to the energetics of the reaction.

In arriving at a rate equation for expressing the evaporation as a function of time we are guided by our finding in the last section. The equation fitted by the data is

$$Q = a\, t^{.9} \qquad (25')$$

in which Q is the cumulative evaporation, a is a parameter which can be evaluated from the data, and t is time. The equation as used in Figures 12 and 13 is in logarithmic form.

On comparing the above equation with the integrated form of the zero order rate equation,

$$(\theta_o - \theta) = k^o\, t, \qquad (20a)$$

wherein $(\theta_o - \theta)$ is the cumulative evaporation, k^o is the rate constant, and t is time, it is apparent that the two equations differ only in the symbology of the proportionality parameter. Since the exponent on time in equation (25') is about 0.9, the zero order rate equation will fit the data satisfactorily if the time period considered is not too long.

In Figure 14 are presented the plots of 5 series A and 5 series B runs according to the zero order rate equation for times up to 27 hours. It is apparent from the figures that deviation from linearity becomes greater as time increases.

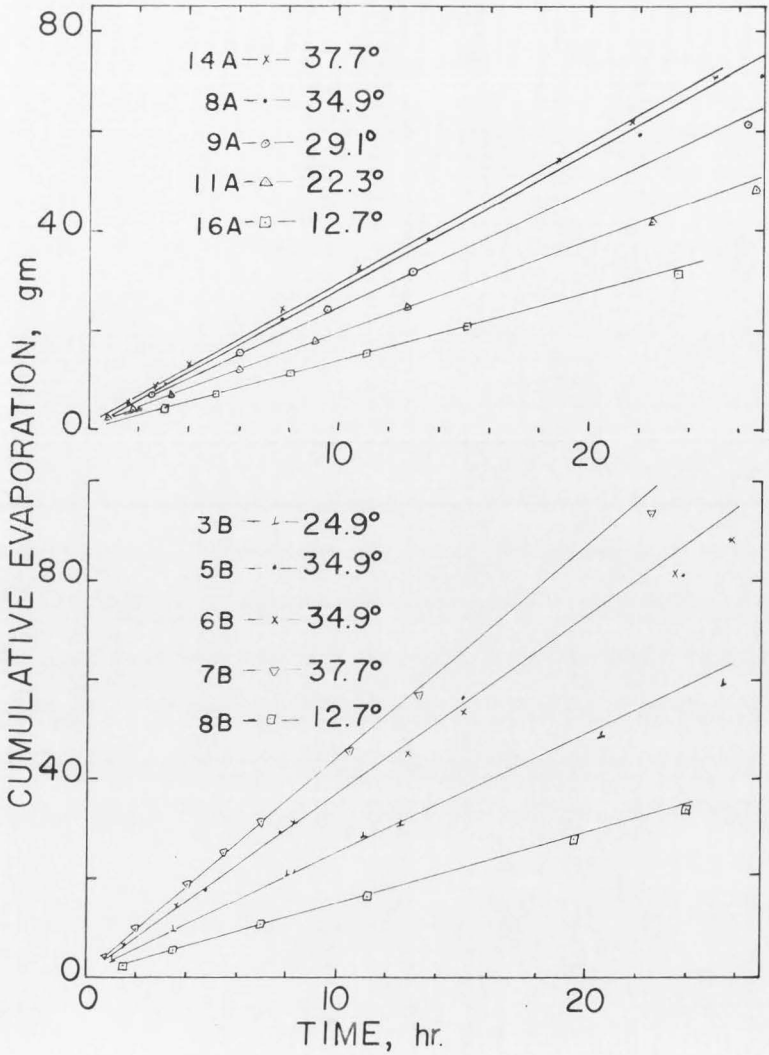

Figure 14. The cumulative evaporation as a function of time plotted according to the zero order rate equation.

In relating the temperature dependence to the energetics of drying the rate constants must be determined for the various runs. The slopes of the plots of Figure 14 are the desired rate constants. Although they may be evaluated graphically, they were determined here by least squares analysis. The values of k^o obtained are presented in Table 8, p. 169.

Once the rate constants were determined, the integrated Arrhenius equation (equation 58, p. 97),

$$\ln k^o = -E^*/RT + \text{constant}, \qquad (58)$$

was invoked. According to this equation, the common logarithm of the rate constant k^o plotted against reciprocal temperature $1/T$ yields a slope which equals $(-E^*/2.30\ R)$. E^* is the activation energy, 2.30 is the conversion factor for natural to common logarithms, and R is the universal gas constant, 1.99 calories per degree Kelvin per mole. The graph of log k^o versus reciprocal temperature for the 5 series A runs of Figure 14 is shown in Figure 15. The slope was again determined statistically.

The linearity of the plot of Figure 15 is very significant. It establishes a very definite relation between the rate constant and temperature, and indicates that the predominant molecular mechanism of the reaction is the same over the temperature range studied.

Runs 8A, 9A, 11A, 14A, 16A $\quad E^* = 5.23 \pm 1.09$ kcal mole^{-1}

Runs 3B, 5B, 6B, 7B, 8B $\quad E^* = 7.24 \pm 1.38$ kcal mole^{-1}

No good explanation for the difference in magnitudes of the activation energies is available. The fact that the upper (series A) and lower (series B) confidence limits overlap slightly indicates that they are not so different statistically. By comparison of their values with those

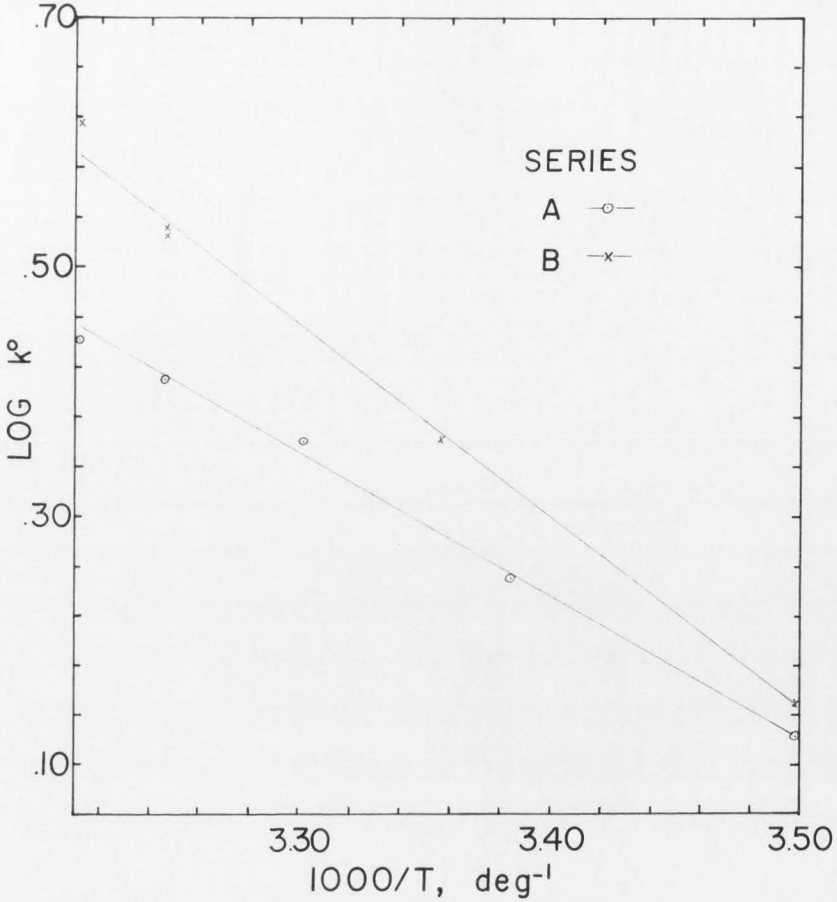

Figure 15. The temperature dependence of the zero order rate constant for several series A and series B runs.

of Table 3, pp. 103-104, it is seen that they are of the same magnitude as for the drying of clay mix (Sherwood and Comings, 1933) and sand (Ceaglske and Hougen, 1937), the drying of wood (Bateman et al., 1939), evaporation from blotting paper (Martin, 1943), and movement of water in heulandite (Tiselius, after Barrer, 1951).

The rates of drying of the soil columns were inconsistent with respect to temperature (see Fig. 16, p. 187) following the slope change of Figures 12 and 13. Evidently real differences in moisture distribution at the time of the slope change and other considerations affecting drying (see p. 190) overshadowed the influence of temperature on the rate of drying. Thus drying did not occur under uniform experimental conditions, other than temperature, with the result that drying during this portion of the drying period can not be validly interpreted in terms of temperature dependence.

DISCUSSION

Determination of Activation Energies

The formal similarity between the empirical moisture flow equation and the zero order rate equation has already been noted. This similarity suggests that the intercept on the evaporation coordinate at unit time should bear the same relationship to the activation energy as do the rate constants determined from the zero order rate law. If the matter is looked into a little further it can be seen that any measurement of the drying process made at the same time on runs at differing temperatures can serve as an index of the temperature dependence of the process. Three different quantities which may be used for the present study are summarized in Table 8: intercept a of the logarithmic form of the empirical flow equation, the cumulative evaporation at 20 hours (about the midpoint of the time interval during which the plots of log Q versus log t are linear), and the reaction rate constants k^{o}. The statistically determined energies of activation obtained, using the data of the 13 runs listed in Table 8, are presented beneath the columns of the various indices of reaction used to obtain them.

The general similarity of the activation energies obtained for the data of Table 8 illustrates the non-critical nature of the index of the reaction as long as it accurately represents the reaction. This fact emerges from two considerations: (i) The logarithm of the quantity which serves as the index of the temperature dependence of the process is plotted against 1/T. Hence the index of reaction carries with it no units which can influence the magnitude of E*; (ii) The activation energies are not

Table 8. The numerical and logarithmic values of three different indices of the drying of the soil columns, and the activation energies associated therewith.

Run	Equil. temp. (°C)	1000/T (°K)	Intercept a		Evap. at 20 hrs.		Rate constant	
			a (gm)	log a	Q (gm)	log Q	k^o (gm/hr)	log k^o
4A	24.9	3.356	1.89	0.2765	35.0	1.5441	0.6405	-0.1935
5A	24.9	3.356	1.05	.0212	35.0	1.5441	1.6940	+ .2289
6A	34.9	3.246	4.70	.6721	58.5	1.7672	2.7843	.4447
8A	34.9	3.246	3.50	.5441	54.0	1.7324	2.5906	.4134
9A	29.1	3.308	3.00	.4771	48.5	1.6857	2.3029	.3623
11A	22.3	3.384	2.75	.4393	38.0	1.5798	1.7828	.2511
14A	37.7	3.216	3.80	.5798	57.0	1.7559	2.7649	.4417
16A	12.7	3.498	1.90	.2788	27.0	1.4314	1.3288	.1235
3B	24.9	3.356	3.10	.4914	49.0	1.6902	2.2957	.3611
5B	34.9	3.246	4.73	.6749	70.0	1.8451	3.3796	.5289
6B	34.9	3.246	4.75	.6767	70.0	1.8451	3.3477	.5248
7B	37.7	3.216	5.23	.7185	84.0	1.9243	4.1522	.6183
8B	12.7	3.498	1.70	.2304	28.5	1.4548	1.4099	.1492
			$E^* = 7.5 \pm 4.3$		$E^* = 6.7 \pm 1.9$		$E^* = 7.4 \pm 4.8$	

absolute quantities, but depend upon the relative effects of temperature within the experiment.

The non-critical nature of the index of the temperature dependence was utilized in obtaining the "experimental" activation energies for evaporation, transpiration, and moisture flow of Table 3. To obtain the activation energies for these experiments it was necessary to find something representative of the experiment to use as the index of temperature dependence. In most cases it was the water loss itself, since this was the information reported most frequently by the researchers. In no case was a rate law explicitly reported from which a rate constant could be calculated.

In the literature of chemistry and physics the most frequently encountered method of expressing rates of reaction of flow of gases and liquids into or through porous materials is through a solution of the

diffusion equation subject to certain boundary conditions. The mathematical solution is the rate equation since it relates the concentration behavior to time. However, apparently because the "mathematics of diffusion" is assumed, there is great emphasis upon determining the diffusion coefficient as a function of temperature and interpreting the results in terms of it.

Since the diffusion coefficient is not amenable to direct measurement it is usually evaluated by measuring the flux as a function of time and dividing it by the other terms in the equation exclusive of the diffusion coefficient. This operational procedure involves making extra calculations, but it does place the expression of the temperature dependence of the reaction in the diffusion coefficient.

In view of the uncertainty in what constitutes diffusion (see pp. 54-55) and in the degree to which the boundary conditions assumed are applicable to the experiment conducted (Barrer and Ibbitson, 1944), it seems quite proper to question the advantage gained in expressing the temperature dependence in terms of changes in the value of the diffusion coefficient when the flux itself would express the temperature dependence. Use of the diffusion coefficient can not be expected to result in any increased accuracy in determining the activation energies, nor can it affect their magnitude. It does furnish a crutch for interpreting the results, since one is conditioned to interpret the results of an activation energy determined by plotting the logarithm of a diffusion coefficient against reciprocal temperature in terms of a "diffusion" process.

In the present experiment, if the interpretation is in terms of the intercept values the question automatically faced is: Is some equilibrium temperature-dependent effect operative which yields the observed results?

In this case the emphasis is on any effect which could limit the initial evaporation. On the other hand, if the cumulative evaporation at a longer time period or the rate constant is the basis of interpretation the first impulse is to consider moisture flow because of the mental association of these quantities with it. So doing amounts to assuming a limiting process, however.

Interpretation of Activation Energies

Background information

There are relatively few interpretations of flow through porous materials as an activated process. Most of these have involved in vacuo adsorption of gases and hydrocarbon vapors (Barrer and co-workers) and steady state and transient flow of gases through porous plugs (Carman and co-workers). The only studies in the soils field appear to be those of Biggar[1], John[2], and Biggar and Taylor (1960). A survey of these studies reveals that the interpretation of activation energies has not stabilized. From the survey of the literature of all fields it is apparent that interpretation of the activated process is made on the molecular level.

Barrer and Rideal (1935) pointed out that the sorption of hydrogen on charcoal is a time process but that the origin of the time dependence has been a matter of dispute. The alternatives include activated diffusion and activated adsorption. In considering the possibilities, Barrer and Rideal state:

> . . .If the time processes are due to diffusion and flow of the type described by Knudsen [Ann. Physik. 28:75 (1909)] we should expect diffusion to obey the Fick law
>
> $$\frac{\partial n}{\partial t} = D \frac{\partial^2 n}{\partial x^2}$$
>
> and also a $\sqrt{T/M}$ relation where T denotes the absolute temperature and M is the molecular mass. If time processes are due to activated diffusion, the equations given by Lennard-Jones [Trans. Far. Soc. 28:333 (1932)], involving an activation energy and consequent large temperature coefficient would hold:
>
> $$\frac{\partial n}{\partial t} = D \frac{\partial^2 n}{\partial x^2} \quad ; \quad \frac{\partial \log D}{\partial T} = \frac{E}{RT^2}$$

---

[1]Biggar, J. W. 1956. On the kinetics of moisture flow in unsaturated soils. Ph. D. Thesis. Utah State University. Logan, Utah.

[2]John, P. T. 1958. Vapor pressure and water movement in the top layers of soil. Ph. D. Thesis. University of Washington. Seattle, Washington.

There is also the more remote possibility of activated adsorption, which for the region where Henry's law is obeyed is described by the expression

$$\frac{\partial n}{\partial t} = k(p_t - p_e) \quad ; \quad \frac{\partial \log k}{\partial T} = \frac{E}{RT^2}$$

(p_t, p_e are gas pressures at time t and at equilibrium).

Activated adsorption has been largely discounted, but activated surface flow remains popular. Carman (1956, pp. 115-128) has given a good summary of both monolayer and multilayer flow. At saturations less than a monolayer, Carman interprets the flow in terms of an apparent surface diffusion coefficient D'_s. (The apparent diffusion coefficient includes the tortuosity effect.) In the multilayer region of adsorption, calculations can be based upon the assumption of either surface diffusion or flow of capillary condensate since both multilayer films and capillary condensate form and there is no way of distinguishing the two experimentally.

If the multilayers are liquid-like one could expect the activation energies to be of about the same magnitude as for self-diffusion in the corresponding liquid. Flood, Tomlinson, and Leger (1952) concluded that the rate-controlling mechanism of flow through the micropore system of carbon rods is a laminar viscous flow of liquid films.

In terms of a more microscopic interpretation of activation energies, Carman (1956, p. 119) states:

> A uniform adsorbent surface does not need to be energetically smooth. A crystalline adsorbent surface possesses a series of regularly spaced sites, at each of which an adsorbent molecule is held more strongly than in the intervening gaps. The surface is said to be uniform because the heat of adsorption is the same for every site; but, as there is an energy barrier between sites, a molecule must gain an activation energy sufficient to enable it to cross the barrier before it can escape to another site. If a molecule gains energy equal to the heat of adsorption, it becomes desorbed, but smaller energies enable it to jump from one site to another without leaving the surface. Surface

> mobility by such a "hopping" motion is quite different from that in a gas and is more nearly akin to diffusion in a condensed phase.
>
> . . . A significant point of difference between diffusion in liquids and diffusion in monolayers, however, must be mentioned. An activated molecule in a liquid is still present in a liquid environment. In a monolayer, activation presumably frees the molecule from localized attachment to the surface, so that its state corresponds to a two-dimensional gas.

Comparison of results

In this study it was proposed to use the activation energies as a clue to the identification of the rate limiting process, rather than with the thought in mind of interpreting the results in terms of a presupposed mechanism.[3] It was for this reason that the "reference" activation energies of Table 2 and the "experimental" activation energies of Table 3 were calculated. The "reference" activation energies of Table 2 reduce the temperature dependence of the various properties of water to a common scale. This is because the activation energies are directly proportional to the sensitivity of the various properties to temperature.

The "experimental" activation energies of Table 3 are to be examined and compared with those of the present study. The experiments exhibiting the most similarity to the experiments of the present study are those for the drying of clay mix (Sherwood and Comings, 1933) and sand (Ceaglske and Hougen, 1937), and the drying of wood (Bateman et al., 1939). All these workers passed air across the drying surface of porous materials under reported conditions of air temperature and humidity.

Sherwood et al. and Ceaglske and co-worker reported results for the period of constant rate of evaporation which is, by general acceptance,

[3] It was hypothesized that liquid phase moisture flow is by some type of surface phase flow; still, however, it was not assumed that moisture flow is rate limiting.

the period of evaporation limited by external conditions. Activation energies calculated from their data range from 4.5 to 7.1 kcal mole^{-1} water.

Bateman and associates (1939) passed air over the sample very rapidly "to insure removal of the moisture from the surface of the specimens as rapidly as it was brought to the surface." The calculated activation energy is 6.1 kcal mole^{-1}. Ceaglske and Hougen (1937) reported data for the falling rate period of drying which yield an activation energy of the same magnitude as they found for the constant rate period (see Table 3, pp. 103-104). The fact that activation energies for experimental conditions indicative of a drying rate limited by flow of moisture within the sample and by external conditions limiting are the same imply that the temperature dependence of drying during these periods are very similar even though the rates may differ. Since the rate of drying during the falling rate period is conditioned by what it was during the constant rate period, external conditions may influence the drying rate during the falling rate period or, conversely, moisture flow influenced the drying rate during the constant rate period.

The close agreement between the activation energies of cited examples from the literature and the present study indicate that activation energies of 4 to 8 kcal mole^{-1} water can be expected for the temperature dependence of drying based on air temperature. Since evaporative drying results in cooling and the evaporative cooling is greater the higher the dry bulb temperature (particularly when humidity is low), activation energies would be somewhat larger if calculations were based on sample temperature instead of air temperature. Sample surface temperatures have been reported by Martin (1943) and by Ceaglske and Hougen (1937). The activation energies

of 5.1 to 6.8 kcal mole^{-1} calculated from data of Martin for evaporation from leaf-shaped blotting paper are also in agreement with those already mentioned.

The activation energies for moisture movement in heulandite found by Tiselius (see Barrer, 1951, pp. 97-103) correspond to activation energies for unsaturated moisture flow in soils such as would occur in movement of moisture to plant roots. The heulandite crystals were, however, found to be anisotropic with respect to moisture flow. Such anisotropy would not be detectable in bulk soil. Barrer (1951, p. 103) states:

> The temperature dependence of the diffusion constants... did not depend appreciably upon the amount of water in the lattice, although we have seen [see Tables 11, 12, and 13, p. 100 of Barrer] that their absolute magnitudes do.

This statement is very revealing in that it suggests that the activation energy for unsaturated flow of moisture in soil may be the same over the entire range of moisture contents of interest in plant growth.

The experiment of Gardner (1959c) and Biggar and Taylor (1960) enable an interesting comparison of the energies of activation for the wetting of soil as compared with those for the drying of soils. Gardner reported the temperature dependence of the weighted mean diffusivity $\bar{D}$ calculated from the moisture distribution in wetted soil columns. The activation energies for his data range from 2 kcal mole^{-1} water for Chino clay to 4 kcal mole^{-1} water for Traver sandy loam. Biggar and Taylor reported activation energies of 1 to 5 kcal mole^{-1} water for infiltration of water into air-dry Millville silt loam soil of various size fractions and bulk densities, and for a range of hydraulic heads on the entering water. The activation energies for the wetting of soil are then consistently lower than those for drying.

In summary of the above comparison, it seems likely that the activation energy for flow of water into porous hygroscopic materials is less than that for drying. With respect to the "reference" activation energies of Table 2, the "experimental" activation energies of this study are intermediate between those for fluid properties of water and the vaporization of water.

Of the remaining experimental activation energies of Table 3, those for the evaporation of liquid water from outdoor tanks (Sleight, 1917) and for transpiration of Ambrosia trifida and Helianthus annuus (Martin, 1943) are in agreement with the temperature dependence of vapor pressure of water. In both cases the evaporation increased exponentially with temperature. The large activation energy for the study of the transpiration of excised leaves in potometers (Kuiper and Bierhuizen, 1959), can not be explained.

The work of Harris and Robinson (1916) of this institution is of considerable interest because of the wide temperature range studied (20 to 90° C) and because one of the soils employed was the same as in this study. Their experimental method was the same at all temperatures yet there is a decided change in slope of plots of evaporation rate versus reciprocal temperature at about 50° C. The result for the data of Harris and Robinson is not unique, however. Kumins, Rolle, and Roteman (1957) observed larger activation energies at temperatures above 60° C in their study of water vapor diffusion through vinyl chloride-vinyl acetate copolymer. The study covered the temperature range 32 to 84° C. These workers could not explain their result in terms of changes in the properties of the copolymer.

Since the two experiments just described were the only temperature dependence studies, involving water or water vapor, encountered in the literature which covered this temperature range and both exhibit unusual behavior, it is suggested that the peculiar behavior of water vapor at about 50 to 60° C in such studies may be real. The only other striking behavior involving water at this temperature of which the writer is aware is that stated by De Vries (1950a). He remarked that, because of the contribution of water vapor flow to the thermal conductivity of soil, at 59° C the thermal conductivity of soil "will be independent of the moisture content." De Vries credits Krischer and Rohnalter (1940) with having first observed this effect. It is not known if there is or is not any correlation between the two effects.

Crank (1956, p. 280) stated that when the diffusivity increases with increasing concentration, as it does for unsaturated moisture flow, "desorption is always slower than sorption." If the lower rate of moisture flow in desorption can be associated with a higher activation energy caused by a greater "resistance" to flow, the results of this study exhibit the proper relation to those available for the wetting of soil (Gardner, 1959c; Biggar and Taylor, 1960).

It must be remembered, however, that (a) little information is available for contrasting mechanisms of flow in drying versus wetting nor of the importance of side effects such as local temperature variations, which, incidentally, are in opposite directions from the equilibrium temperature in the two cases, and (b) Crank was comparing absolute magnitudes whereas the activation energies depend not upon absolute values of moisture flow, but upon relative sensitivity of flow to temperature. If fluid properties dominate flow the temperature dependence of wetting

should parallel that of the fluidity (reciprocal viscosity) of water, and the sensitivity of evaporative drying to temperature should correspond more closely to that of the temperature dependence of vapor pressure of water. The results of Gardner (1959c) do suggest that the barrier giving rise to the activation energy of wetting is similar in soil water and free water. The results of the present study are intermediate in magnitude between those expected for evaporation of free water and properties of liquid water. This suggests that the activation energy of drying may be influenced by the activation energies of both vaporization and unsaturated moisture flow.

Parabolic Moisture Distribution

In the review of literature it was concluded that the parabolic moisture distribution for drying is characteristic of hygroscopic, porous materials with appreciable colloidal character. The implications of the parabolic moisture distribution are several. One practical application is to fallowing. Field soil dries in general agreement with the parabolic distribution. The moisture content is lowest at the soil-air interface and increases with depth, but the moisture content does not increase linearly with depth. Instead there is a shallow layer of soil in which the moisture content increases rapidly with depth; below this layer the moisture content increases more gradually with depth in the soil profile.

It appears that moisture conservation in fallowing is mainly a result of the influence of the shallow dry layer. It transmits liquid water very slowly to negligibly by unsaturated flow. Once it forms, moisture transfer through it is predominantly by molecular diffusion of the water vapor. The dry soil is also a barrier to this process. (Recall the review of literature conclusion that a layer of soil of equilibrium dryness of a few mm in thickness introduces vapor diffusion as the rate controlling process in drying.)

If moisture loss is controlled by the moisture status of a relatively thin surface layer, which is consistent with experience, the parabolic moisture distribution suggests that attempts to relate the rate of moisture loss with moisture distribution must involve a large number of measurements very near the soil surface. This requires more careful and more extensive moisture sampling than is usually done. If instrumental methods are used to follow the moisture changes they must be microscopic and accurate.

Solutions of the diffusion equation with diffusivity moisture content dependent predict roughly a parabolic moisture distribution with distance from the drying surface. The diffusion equations have been the most successful method to date for predicting moisture distributions and rates of water flux in soil moisture movement. This approach places the emphasis on the dependence of soil moisture diffusivity on moisture content. In contrast, more mechanistic approaches emphasize the apparent driving forces to which the macroscopic fluxes are unexplainedly found to be not directly proportional. The lesser success of the mechanistic approaches suggests that the microscopic flow processes are all important and that these may be more accurately represented by the sensitivity of diffusivity to moisture content than by the dependence of the macroscopic flux on the driving force.

Sherwood (1932) found that the parabolic moisture distribution develops in soil even during the period of constant rate of evaporation, that is, even during that period of time in which external drying conditions rather than moisture flow within the sample is limiting the rate of drying. The parabolic distribution is also observed in the drawdown of the water table with radial distance from pumped wells in non-steady flow (Peterson, 1957, p. 203).

From the above cited cases and the present results it is concluded that the parabolic distribution is not unique for a particular moisture condition but general from practically saturation on through moisture conditions of the plant growth range. The same experiments suggest that the parabolic distribution is not a function of the method of inducing flow.

The parabolic distribution also seems to dominate over temperature

effects under isothermal conditions. In physical adsorption the amount of gas or vapor adsorbed is greater the lower the temperature. In the present study there was an appreciable temperature gradient across the surface few cm of soil. If water were moving in the vapor phase through the drying surface layer it would have tended to be adsorbed in increasing amount as the surface was approached since the surface of the soil column was cooler than any other point in the sample.

The evidence is good then that the parabolic moisture distribution is a unique function of the moisture flow process, and that it can be expected for a wide saturation range if liquid phase moisture flow is dominant. It is apparently the natural response of a desaturating porous medium in coming to equilibrium with the driving force of flow.

The importance of the flow coefficient serves as the stepping stone to another idea: In the operational method of determining the capillary conductivity of soil water by dividing the flux by the moisture potential gradient (Richards and Weeks, 1953; Richards et al., 1956), it is apparent that the capillary conductivity so determined always lags behind its real value. The reason for this is simple. The moisture conductivity has to change before the moisture distribution can change, and since calculations depend upon finite intervals of change in the moisture potential gradient (except for the steady state flow case in which both the flux and the potential gradient remain constant, a case which is extremely rare if nonexistent for unsaturated flow) the capillary conductivity will have changed again before the potential gradient could change. The operational method is useful for approximating the true value of the capillary conductivity only when the moisture potential gradient is allowed to change by very small increments.

The above remarks all point to the need for a better understanding of the microdynamics of the flow process. The mechanism of flow is difficult to pinpoint, but it undoubtedly consists of a conglomeration of molecular processes some of which are statistical mechanically liquid-like while others are more gas-like. It is suggested that it can be visualized as occurring in a surface phase which may exhibit discontinuities and that it may be aided by auxiliary mechanisms such as molecular hopping.

Parabolic Law

In his chapter IX which deals with surface reactions of metals, formation of protective layers and related reactions, Jost (1952) discusses the "parabolic law" describing the formation of the tarnished layer in the reaction of various gases with metals. If it is assumed that diffusion through the layer of oxide or other compound is the rate determining step in the tarnishing reaction (the rate of reaction at some interface could be rate controlling) and if the increase in thickness of the layer x is chosen as measure of the reaction velocity, one can write

$$dx/dt = k/x.$$

This expression indicates that the rate of increase of the layer will be inversely proportional to the thickness of the layer, "because the concentration gradient in the layer will be proportional to 1/x, provided we have a quasi-stationary state...." (Jost, 1952, p. 341). The constant k is proportional to the diffusion coefficient.

On integration

$$x^2 = 2\,k\,t$$

is obtained if the thickness of the layer is zero at time zero. This is the "quadratic" law which, according to Jost, was first derived by Tammann in 1922.

Barrer (1951, p. 50) points out that solutions of the diffusion equation involving semi-infinite and infinite solids all give the concentration as function of the dimensionless group $x/\sqrt{Dt}$ wherein x is the distance from a boundary of interest, D is the diffusion constant, and t is time. Squaring the dimensionless group yields the relation between t and x of the parabolic law. Barrer (1951, p. 98) used the relationship

of the parabolic law to obtain the diffusion constants of water in the experiments of Tiselius.

The parabolic relationship can be applied to the data of this study. In so doing it is only necessary to plot the relationship between the distance the tensiometers are from the soil surface squared against the time at which a given soil moisture suction is indicated at various distances from the surface. When the data of run 11A given in Figure 10, p. 153, was tested by plotting x^2 (4, 16, 64, 256, 900 cm^2) against the time t (7.1, 8.9, 11.8, 22.5, 66 hours) required for a soil moisture suction of 10 cm Hg to develop at the respective depths, the plot was linear.

This result is of some interest because it suggests the possibility of obtaining ideas concerning interpretation of the rate of evaporation as a function of water table depth or mulch depth from published papers on rates of corrosion of metal as a function of corrosion layer thickness.

That the analogy between corrosion layers on metals and "protective" dry layers in evaporative loss of moisture from soil is not mere fancy is illustrated by the statement of Philip (1957b) who expressed his understanding of evaporation as a function of depth to the water table as follows:

> Amongst the complex of related factors such as the decrease of moisture gradients and of D, perhaps the most distinctive feature is the growth of a surface soil layer in which moisture transfer is predominantly by vapor diffusion--in other words the laminar sub-layer is virtually thickened (for the purposes of moisture transfer) by extension into the soil, and this constitutes a bottleneck not present when the water table is shallow.

Philip's rational interpretation of the limiting process in terms of vapor diffusion was inferred from the circumstances. It was not supported by any direct experimental evidence on vapor diffusion.

The data of Figure 16, in which the behavior of the rate of evaporation is shown as a function of time for several series B runs, serve as a basis for discussing the possible limiting processes during various periods of the drying of the soil columns of this study. The plateau region which covers the time interval zero to about fifty hours is the period of evaporation limited by external drying conditions. Thereafter the rate of evaporation decreases rapidly for a time. During this time the rate of evaporation is probably limited by the rate of unsaturated flow of moisture to the sites of evaporation. At long times the evaporation rate decreases very slowly. During this time period the rate of evaporation is evidently limited by the rate of diffusion of water vapor through the dry surface layer. Run 8B of Figure 16 is exceptional. The temperature of this run was 12.7° C and indications are that external drying conditions limited the rate of moisture loss for a considerably longer time period than in the cases of the other runs.

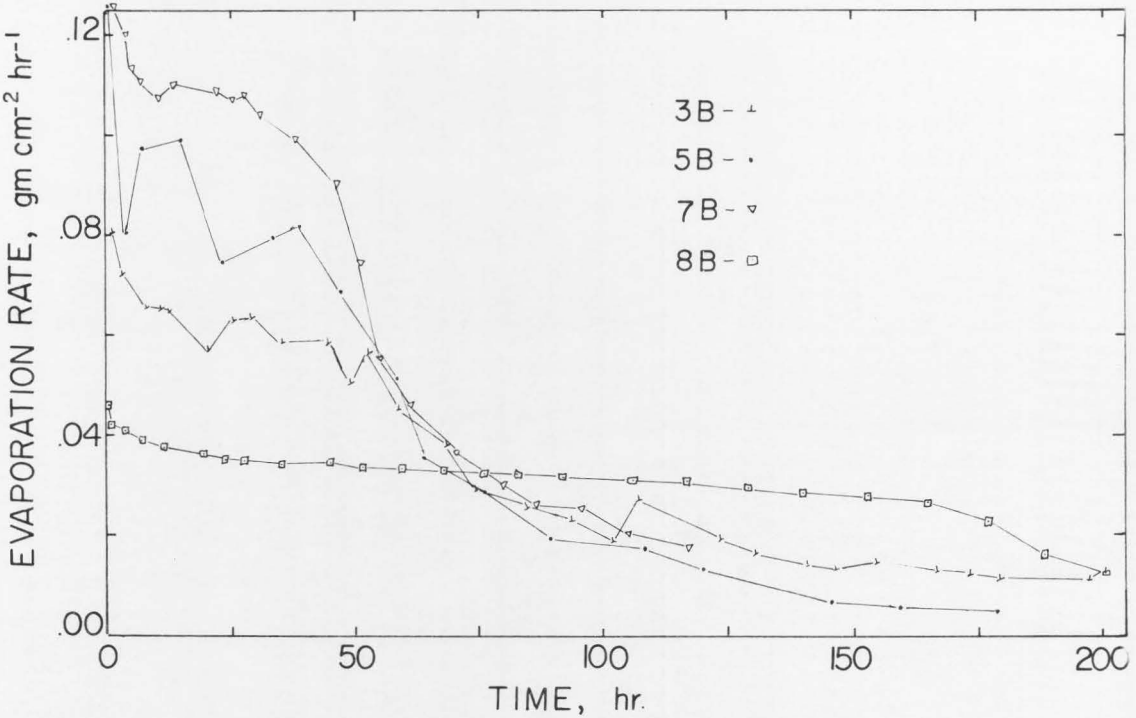

Figure 16. Rate of evaporation as function of time.

Heat Transfer

In the theory section, two methods of considering heat transfer were suggested. One method required the calculation of the heat transfer coefficient. This was not done, however. The data of Figures 4 and 5 show why. These figures suggest that calculated heat transfer coefficients would change continuously until the linear relationship between the evaporation rate and temperature depression to the right of the maxima occurred. Thereafter the heat transfer coefficients should remain essentially constant. It would still not be known how to interpret them in a meaningful way. It should be pointed out, however, that the data of all runs would be expressed by a common, directly comparable parameter. By the method of its determination it would have the same significance as any phenomenological coefficient determined empirically by dividing a flux by a driving force.

The other suggested heat transfer information, that based on thermal properties of the soil, would be much more difficult to obtain for the present experiments and would be considerably less accurate than the calculated heat transfer coefficients. The difficulty in this case arises from two main sources--(a) the great number of assumptions required due to lack of independent characterization of the thermal properties of Millville silt loam, and (b) the complicated geometry of the system studied. The geometry of the present system is that of heat flow through the walls of a cylinder and out one end.

Flow Sheet of Analysis

The results of the present study correspond most closely to the hypothetical cases two and three of the flow sheet of analysis, p. 109.

In case two it was hypothesized that if (a) the temperature stayed low for a while, then climbed back to the temperature of the air passing over the sample, (b) the moisture were distributed parabolically with distance from the evaporating surface, and (c) the evaporation rate decreased continuously from the beginning of the experiment, the evidence is that the evaporation conditions change during the experiment and that moisture flow is of a diffusion type. These conditions are the ones which most of the runs fit. The conclusions were based on knowledge that the evaporation conditions with reference to the sample do change any time the temperature and humidity conditions are not constant throughout the experiment, and that the moisture distribution is compatible with predictions of the mathematics of diffusion.

In case three of the flow sheet of analysis it was hypothesized that if (a) the temperature stayed low for a while, then climbed back to the temperature of the air passing over the sample, (b) the moisture distribution changes for a while then approaches a steady state, and (c) the evaporation reaches a steady rate, then the evaporation rate will be low and the rate of evaporation is governed by moisture distribution. Conditions (b) and (c) are actually closely approximated after several days by most of the runs since both the moisture distributions and the evaporation rates change slowly once the surface few cm of the sample have become quite dry. Once this condition is achieved the evidence is good that the rate of evaporation is controlled by the moisture distribution.

About the Experiment

Sources of difficulty and error

Several aspects of the present study combined in such a way as to make the experiment somewhat less than ideal. One source of error of some importance is associated with the fact that the soil column shrank on drying from its initial moisture content. This shrinkage away from the walls of the container amounted to about 0.5 mm in the most extreme cases, but shrinkage was not uniform. The largest crack was always at the uppermost surface of the horizontal soil columns. It could cause a change in the magnitude of heat conduction from the temperature bath to the sample and could also cause assymetry in the flow of heat within the sample. It could affect vapor moisture transfer directly by providing an air crack between the sample and the container wall in which free diffusion of the water vapor could occur.

This source of error makes it fortunate that the differences in temperature distribution and shrinkage had little or no apparent effect on the evaporation behavior during the early part of the experiments. It was the main factor in the decision not to analyze the moisture flow data intensively beyond the point of the slope changes of Figures 12 and 13.

Another source of error involved the unexplained behavior of the silica gel of the water vapor traps to spontaneously gain about 0.10 gm in weight between the time it was placed in the drying column and the time it was inserted in the air flow line. The weight change during weighing was negligible, and the magnitude is too great to be accounted for directly by absorption of the water vapor of the container into which it was poured. It is also considered hysteresis-independent because of the good reproduc-

ibility of the dry weight and the results of such workers as Rao (1941). Rao found remarkable stability of the scanning curves on repeated absorption-desorption of water vapor by silica gel. The maximum error from this source is not more than 2 to 3 per cent. It becomes progressively larger during the course of the experiment because the rate of evaporation decreased with time whereas the spontaneous weight gain remained constant. The data reported in Appendix I was not corrected.

The nature of the operation of tensiometers causes difficulty in such an experiment. They must give up water to the sample in order to register a moisture change. There were five tensiometers embedded in the soil columns of the series B runs and seven in the columns of the series A runs. What is easily overlooked is the volume of water the tensiometers contain. In one case the amount of water required to fill the five tensiometers and the associated tubing of the series B soil column was measured and found to be about 160 ml.

When the tensiometers become inoperative they continue to lose water and unless clamped off will completely drain. This source of water within the sample can cause deviation from any assumed relationship between cumulative evaporation and time, either empirical or theoretical. In this experiment it could affect the time of the slope change of the plots of Figures 12 and 13.

The evidence is good that the water absorbed by the soil from a given tensiometer distributed itself in response to the moisture pattern dominated by the mechanism of flow. This is supported by the smoothness of the moisture sampling curves of Figure 9. They show no discontinuities at the depths at which the tensiometers were inserted. It is also supported by the general smoothness of the temperature-time curves of Figures

2 and 3. Both temperature and suction measurements were made at the 2 and 4 cm depths. If sporadic evaporation had occurred at these depths it would have been reflected in more inconsistent temperature measurements at these depths.

Whereas the water loss by the tensiometers did not change the suction pattern it could have affected the cumulative evaporation somewhat by altering the boundary conditions of flow. The evaporation of moisture was apparently mainly a function of the moisture status of the first few cm of sample depth, however. It is believed that the rate of unsaturated flow through this zone governed the evaporation rate and that the interpretation of the moisture flow data is valid.

When run 8B was terminated, a streak of darker soil was noticed across the surface of the soil column. The dark streak was narrow at the inlet and outlet points of the air and broadened symmetrically toward the center of the column. The soil column was dissected in 1 cm increments and the electrical conductivity of the saturation extract was determined. The results obtained are shown in Figure 17. The first four surface cm of soil exhibit an osmotic pressure of the saturation extract which could be considered different from that of the remainder of the soil column. The first 1 cm increment of soil exhibits an osmotic pressure of 1.79 atmospheres, or three times that of the second 1 cm increment of soil. The salt distribution indicates that the evaporation occurred principally in the first cm layer of soil and that probably very little evaporation occurred below 4 cm.

The soil column of run 8B was used also in the previous run, 7B. The combined cumulative evaporation for these runs converted to equivalent surface depth of water shows that nearly 14 cm of water passed through

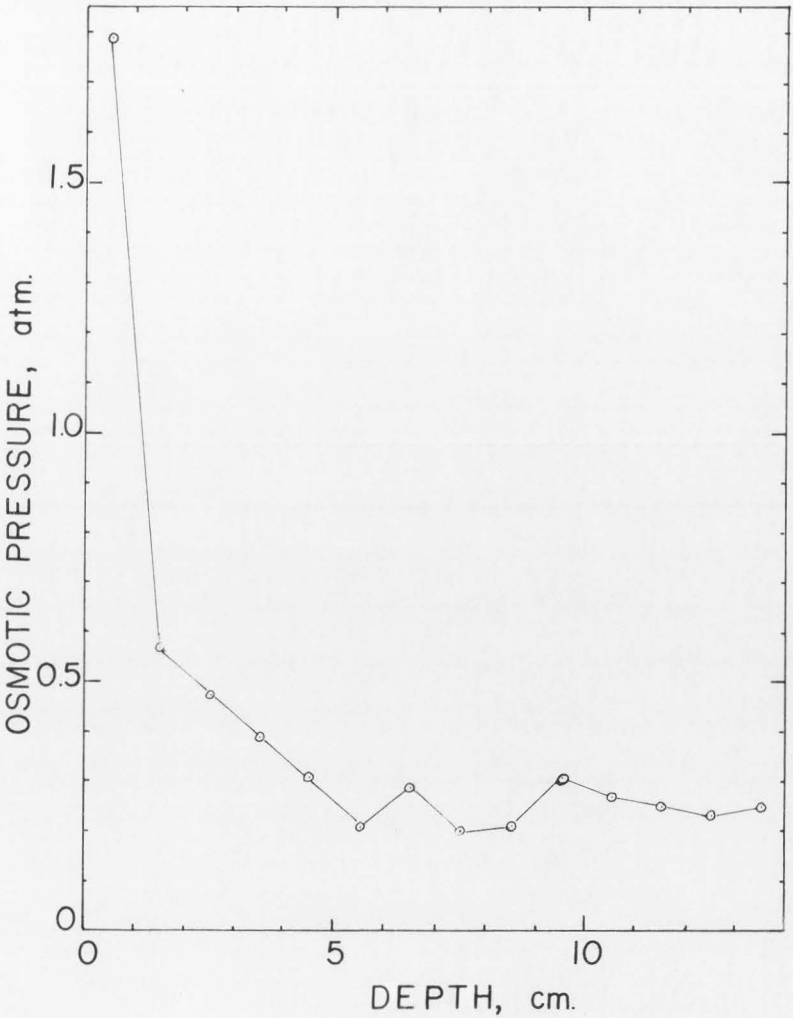

Figure 17. The osmotic pressure of the saturation extract of the soil column of runs 7B and 8B.

the surface of the column during these two runs. Since the soil columns were always wetted with distilled water the salt accumulated was entirely that of the soil solution.

The solute accumulation in the surface layers of soil may have had a slight influence on the results of these experiments.

Suggestions for future studies

The experience of this study prompts certain suggestions for similar future studies. They include the use of a sample container with better and better known thermal properties than lucite. The thermal properties and shrinkage behavior of the soil used should be studied independently of the experiment in which they become major considerations in interpretation of results.

For aiding in making heat transfer calculations, in particular, a system of simpler geometry should be employed.

CONCLUSIONS

The equilibrium temperature had an important influence on the drying rate, but the temperature distribution resulting from evaporative cooling did not.

The initial rate of drying of the soil columns was limited by external drying conditions. After about two days moisture transfer within the soil columns became rate limiting.

A parabolic distribution of moisture with respect to the interface of extraction is characteristic of soil. In agreement with it, moisture flow is dominated by conditions near the interface. The parabolic distribution is in good qualitative agreement with solutions of the diffusion equation.

The equation $Q = a\ t^b$ successfully describes the time dependence of the drying of soil.

Little success can be expected of attempts to relate the evaporative loss of moisture from soil to the instantaneous distribution of moisture in the soil.

The activation energies of 4 to 8 **kcal** $mole^{-1}$ water found in this study are in good agreement with those calculated from the literature for cases in which the temperature dependence of the drying of various porous media was studied. The apparent activation energies are intermediate between those for the fluid properties of free water and the latent heat of vaporization of water.

SUMMARY

Experiments were conducted to gain information on the rate limiting process or processes in the drying of soil. The temperature and moisture distributions were measured in soil columns dried by passing air over their surfaces. The experiments were carried out at temperatures ranging from 12.7° to 37.7° C using two sizes of soil columns. The Arrhenius theory was applied to the data in order to obtain the activation energies for the drying process from its temperature dependence. The results were compared with activation energies for various properties of pure water and with activation energies for evaporation, transpiration, and moisture flow calculable from the literature.

Not all experiments behaved the same with respect to the temperature distributions resulting from evaporative cooling, but the drying of all runs was expressible by the equation $Q = a\ t^b$ wherein Q is the cumulative evaporation, t is time, and a and b are constants. The average value of b for all runs was 0.91 for about the first two days of drying. The slope then changed and the average value for b for all runs was 0.47. The parameter a was a function of equilibrium temperature. The values of b and other evidence indicate that the initial rate of evaporation was limited by external drying conditions. After the slope change moisture flow within the soil columns limited the rate of evaporation.

The activation energy calculated from the Arrhenius theory for the period of time up to the slope change was 5.23 ± 1.09 kcal $mole^{-1}$ water for one set of experiments and 7.24 ± 1.38 kcal $mole^{-1}$ water for another set of experiments. By comparison with activation energies available from data in the literature, activation energies of this magnitude appear

to be characteristic of the drying of porous materials. The activation energies indicate a mechanism of flow which exhibits characteristics of both liquid and gaseous phase molecular processes.

The moisture distribution measured by the tensiometers could not be quantitatively related to the evaporation rate, but the tensiometer readings and direct gravimetric sampling revealed a parabolic distribution of the moisture with distance from the drying surface. This moisture distribution is apparently characteristic of the desaturation of soil. It has important implications in many unsaturated flow phenomena including moisture flow to roots and to wells, and fallowing. It also throws doubt on the rigor of assumed infinite and semi-infinite boundary conditions for sample thicknesses practical in laboratory experiments.

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APPENDIX I

Summarized Thesis Data

Table 9. Run 4A. Basic data on the evaporation of water from the soil column and its replenishment from the "water table."

Day	Hour of day	Time since last reading Δt (hrs)	Time since expt. began (hrs)	Water evaporated ΔQ (gms)	Rate of evaporation $\Delta Q/\Delta t$ (gm/hr)	Running total of evap., Q (gms)	H_2O uptake from reservoir (cc)	Rate of H_2O uptake by sample (cc/hr)	Running total of uptake (cc)
9-9-58	1200		0.00						
	1230	0.50	0.50						
	1415	1.75	2.25	4.1	1.82	4.1			
	1700	2.75	5.00	4.8	1.75	8.9			
	1930	2.50	7.50	4.1	1.64	13.0			
9-10-58	0006	4.60	12.10	8.9	1.93	21.9			
	0800	7.90	20.00	13.1	1.66	35.0			
	1300	5.00	25.00	8.3	1.66	43.3			
	1700	4.00	29.00	6.8	1.70	50.1			
	2000	3.00	32.00	5.0	1.67	55.1			
9-11-58	0800	12.00	44.00	19.1	1.59	74.2			
	1500	7.00	51.00	12.5	1.79	86.7			
		At 1500 began to measure uptake of water from end reservoir by soil sample							
	2000	5.00	56.00	8.2	1.64	94.9			
9-12-58	0806	12.10	68.10	16.5	1.36	111.4			
	1700	8.90	77.00	14.4	1.62	125.8			
	2130	4.50	81.50	7.3	1.62	133.1			
9-13-58	0945	12.25	93.75	18.1	1.47	151.2			
	1645	7.00	100.75	10.2	1.46	161.4			
9-14-58	0900	16.25	117.00	25.1	1.54	186.5			
	2000	11.00	128.00	15.7	1.43	202.2			
	2300	3.00	131.00	5.1	1.70	207.3			
9-15-58	0930	10.50	141.50	16.7	1.59	224.0			
	1015						120	1.39	120
	1600	6.50	148.00	11.2	1.72	235.2			
	2145	5.75	153.75	8.6	1.50	243.8			
9-16-58	0945	12.00	165.75	16.4	1.37	260.2			
	1700	7.25	173.00	12.0	1.65	272.2			

9-17-58	0727	14.45	187.45	20.5	1.42	292.7			
	2354	16.45	203.90	24.5	1.49	317.2			
9-18-58	0924	9.50	213.40	14.0	1.47	331.2			
	1430	5.10	218.50	7.6	1.47	338.9			
	2100	6.50	225.00	9.5	1.46	348.4			
9-19-58	0845	11.75	236.75	17.2	1.46	365.5			
	1500	6.25	243.00	9.5	1.52	375.0	140	1.39	260
	2200	7.00	250.00	9.9	1.41	384.9			
9-20-58	0930	11.50	261.50	16.4	1.43	401.3			
	1500	5.50	267.00	8.2	1.48	409.5			
	2300	8.00	275.00	10.2	1.27	419.6			
9-21-58	1415	15.20	290.20	22.3	1.47	442.0			
	1805	3.88	294.08	5.5	1.42	447.5			
9-22-58	0918	15.22	309.30	22.1	1.45	469.6			
	1700	7.70	317.00	11.0	1.43	480.6			
9-23-58	0000	7.00	324.00	10.2	1.60	490.8			
	1000	10.00	334.00	13.4	1.34	504.1			
	1645	6.75	340.75	9.1	1.35	513.2			
	2300	6.25	347.00	9.4	1.50	522.6	165	1.59	425
9-24-58	0830	9.50	356.50	13.0	1.36	535.5			
	1606	7.60	364.10	12.2	1.60	547.7			
	2300	6.90	371.00	10.2	1.47	557.8			
9-25-58	0936	10.60	381.60	14.84	1.40	572.67			
	1706	7.50	309.10	9.90	1.32	582.57			
9-26-58	0845	15.65	404.75	15.75	1.01	598.32			
	1700	8.25	413.00	11.00	1.33	609.32			
9-27-58	0038	7.63	420.63	10.45	1.37	619.77			
	0721	6.72	427.35	8.63	1.28	628.40			

Table 10. Run 4A. The distribution of moisture in the soil column as a function of time and distance from the evaporating surface.

Day	Hour of day	Tensiometer Readings (cm Hg at porous cups at given dist. from evaporating surface) 2 cm	4 cm	8 cm	16 cm	24 cm	30 cm
9- 9-58	1200	4.4	4.2	4.4	4.6	4.4	4.3
	1230	4.6	4.8	5.0	4.7	4.3	4.1
	1415	6.1	6.7	6.6	5.8	4.5	5.1
	1700	7.4	7.4	7.3	6.7	5.9	5.4
	1930	7.7	7.7	7.5	7.0	6.1	5.6
9-10-58	0006	8.2	8.0	7.9	7.3	6.4	5.8
	0800	8.7	8.5	8.3	7.7	6.7	6.2
	1300	10.0	8.8	8.5	8.0	6.9	6.4
	1700	10.0	8.7	8.5	7.9	6.9	6.4
	2000	10.0	8.6	8.5	8.0	6.9	6.4
9-11-58	0800	9.2	9.1	8.8	8.2	7.3	6.7
	1500	9.7	9.4	9.2	8.6	7.5	6.9
	2000	9.7	9.5	9.2	8.6	7.5	6.9
9-12-58	0806	10.3	10.1	9.9	9.2	8.1	7.5
	1700	10.6	10.3	10.1	9.5	8.3	7.6
	2130	10.6	10.3	10.1	9.5	8.2	7.6
9-13-58	0945	10.7	11.2	10.9	10.2	8.9	8.4
	1645	11.4	11.1	10.9	10.1	8.9	8.4
9-14-58	0900	12.1	11.9	11.7	11.0	9.7	9.1
	2000	12.5	12.3	12.0	11.2	9.9	9.4
9-15-58	0930	13.2	13.0	12.6	11.8	10.4	9.7
	1600	13.4	13.2	12.9	12.0	10.5	9.7
	2145	13.5	13.3	12.9	12.2	10.6	10.1
9-16-58	0945	14.0	13.7	13.4	12.5	11.0	10.4
	1700	14.4	14.1	13.7	12.7	11.3	10.6
9-17-58	0727	15.1	14.8	14.3	13.4	11.9	11.2
9-18-58	0924	16.6	16.2	15.8	14.7	12.9	12.1
	1430	16.6	16.2	15.8	14.7	12.9	12.1
	2100	16.8	16.5	16.0	14.9	13.2	12.1
9-19-58	0845	17.2	16.7	16.3	15.1	13.3	12.3
	2200	17.5	17.1	16.6	15.2	13.4	12.3
9-20-58	0930	17.7	17.4	17.0	15.6	13.7	12.6
	1500	18.1	17.8	17.4	15.9	14.0	13.0
	2300	18.9	18.5	18.0	16.3	14.3	13.3
9-21-58	1415	19.9	19.5	19.0	17.0	14.9	13.8
	1805	20.0	19.5	19.1	17.0	14.9	13.8
9-22-58	0918	20.8	20.4	19.9	17.4	15.1	14.0
	1700	21.2	20.7	20.3	17.4	15.0	14.0
9-23-58	0000	22.1	21.8	21.5	17.1	14.6	14.0
	1000	24.7	24.5	24.1	16.1	13.9	13.5
	1645	27.1	26.6	26.0	15.9	13.2	12.6
	2300	28.8	28.0	27.1	14.3	12.0	11.2

Table 10. Continued.

Tensiometer Readings

Day	Hour of day	(cm Hg at porous cups at given dist. from evaporating surface) 2 cm	4 cm	8 cm	16 cm	24 cm	30 cm
9-24-58	0830	31.5	30.1	28.4	13.9	11.9	11.2
	1606	36.1	34.6	31.5	13.8	11.9	11.3
	2300	40.8	38.6	34.0	13.8	12.2	11.5
9-25-58	0936	48.2	44.5	38.6	13.0	11.5	11.1
	1706	52.1	48.0	42.0	12.3	10.9	10.7
9-26-58	0845	56.2	52.8	48.0	11.5	10.4	10.0
	1700	56.5	53.8	50.2	10.9	9.7	9.6
9-27-58	0721		54.6	54.6	10.3	9.3	9.0

Table 11. Run 4A. The distribution of temperature in the soil column as a function of time and distance from the evaporating surface.

Day	0.5 cm		5.0 cm		10 cm		16 cm	
	Hour	Temp. (°C)	Hour	Temp. (°C)	Hour	Temp. (°C)	Hour	Temp. (°C)
9- 7-58	1318	24.9	1319	24.9	1322	24.9	1323	24.9
9- 9-58	1154	24.9	1155	24.9	1156	24.9	1157	24.9
	1224	21.9	1226	24.1	1227	24.9	1228	24.9
	1255	19.3	1256	23.3	1257	24.7	1259	24.9
	1417	18.7	1432	22.9	1433	24.4	1434	24.8
	1703	18.7	1705	22.8	1705	24.3	1706	24.8
	1924	18.9	1925	22.8	1926	24.3	1926	24.8
9-10-58	0009	19.1	0010	22.8	0011	24.3	0012	24.8
	0747	18.8	0748	22.8	0748	24.3	0749	24.8
	1349	18.8	1350	22.7	1351	24.3	1352	24.7
	1950	19.0	1952	22.8	1953	24.3	1953	24.8
9-11-58	0805	19.0	0806	22.9	0806	24.3	0807	24.8
	1453	19.1	1452	22.9	1452	24.3	1451	24.8
	1958	19.1	1958	22.9	1959	24.4	2000	24.8
9-12-58	0810	19.2	0811	22.9	0811	24.4	0812	24.8
	2125	19.2	2124	22.9	2123	24.4	2122	24.8
9-13-58	0940	18.7	0740	22.9	0941	24.3	0942	24.8
9-14-58	0858	19.5	0857	22.9	0856	24.2	0856	24.5
	2005	19.7	2006	23.0	2008	24.4	2009	24.8
9-15-58	0937	19.3	0939	22.9	0938	24.4	0938	24.8
	1600	19.1	1600	22.8	1602	24.3	1603	24.7
	2156	19.7	2157	22.9	2157	24.4	2158	24.8
9-16-58	0920	19.4	0920	22.8	0919	24.3	0919	24.6
	1658	19.4	1659	22.9	1659	24.4	1659	24.8
9-17-58	0723		0724	22.8	0725	24.4	0725	24.7
9-18-58	0923	19.2	0924	22.8	0926	24.2	0926	24.7
	1432	19.0	1433	22.8	1433	24.3	1436	24.7
9-19-58	0850	20.3	0855	23.0	0856	24.5	0857	24.7
	2210	19.4	2211	22.9	2212	24.4	2212	24.8
9-20-58	0925	19.6	0926	22.9	0926	24.3	0927	24.8
	1504	19.4	1505	22.7	1508	24.3	1508	24.7
	2255	19.4	2256	22.6	2257	24.2	2258	24.5
9-21-58	1419	19.4	1419	22.9	1420	24.4	1420	24.8
9-22-58	0921	19.4	0922	22.8	0923	24.3	0923	24.7
9-23-58	0951	19.6	0952	22.9	0953	24.3	0953	24.8
	2303	19.5	2304	22.8	2304	24.3	2305	24.8
9-24-58	0832	19.2	0833	22.8	0833	24.3	0834	24.8
	2306		2309	22.7	2310	24.3	2310	24.8
9-25-58	0936	19.4	0939	22.9	0940	24.3	0940	24.8
	1710	19.6	1711	22.9	1712	24.4	1712	24.8
9-26-58	0850	19.6	0851	22.9	0851	24.3	0852	24.7
9-27-58	1742	20.2	1743	23.2	1744	24.4	1745	24.7

Table 12. Run 5A. Basic data on the evaporation of water from the soil column and its replenishment from the "water table."

Day	Hour of day	Time since last reading Δt (hrs)	Time since expt. began (hrs)	Water evaporated ΔQ (gms)	Rate of evaporation $\Delta Q/\Delta t$ (gm/hr)	Running total of evap., Q (gms)	H_2O uptake from reservoir (cc)	Rate of H_2O uptake by sample (cc/hr)	Running total of uptake (cc)
10-17-58	1238		0.64	1.35	2.11	1.35			
	1401	1.38	2.02	2.57	1.86	3.92			
	1656	2.91	4.93	5.25	1.80	9.17			
	2300	6.07	11.00	10.30	1.70	19.47			
10-18-58	0045	1.75	12.75	3.07	1.75	22.54			
	1030	9.75	22.50	16.02	1.64	38.56			
	1300	2.50	25.00	4.26	1.70	42.82			
10-19-58	0206	13.10	38.10	18.79	1.43	61.61			
	1836	16.50	54.60	25.77	1.56	87.38			
	1948						-19.0[a]	-0.34[a]	-19.0[a]
	2345	5.15	59.75	8.00	1.55	95.38			
10-20-58	0949	10.07	69.82	15.72	1.56	111.10			
	1536	5.78	75.60	9.10	1.57	120.20			
	2300	7.40	83.00	11.12	1.50	131.32			
10-21-58	0830	9.50	92.50	15.15	1.59	146.47			
	1400	5.50	98.00	8.36	1.52	154.83			
	1415						-17.0	-0.40	-36.0
	1939	5.65	103.65	9.20	1.63	164.03			
10-22-58	0836	12.95	116.60	19.96	1.54	183.99			
	1424	5.80	122.40	8.69	1.50	192.68			
10-23-58	0000	9.60	132.00	13.20	1.37	205.88			
	1000	10.00	142.00	14.35	1.44	220.23			
	1700	7.00	149.00	10.00	1.43	230.23			
10-24-58	1000	17.00	166.00	24.22	1.42	254.45	0.0	0.0	0.0
	1700	7.00	173.00	10.02	1.43	264.47			

10-25-58	1115	18.25	191.25	25.84	1.42	290.31
	1500	3.75	195.00	5.46	1.46	295.77

[a]An amount of water greater than put into the reservoir was being removed. Suction data and distribution of moisture as determined by sampling the column indicate water was leaking into the column at the tensiometer 12 cm from the surface. Data is viewed as reflecting an effectively shorter soil column than the actual 31 cm column used.

Table 13. Run 5A. The distribution of moisture in the soil column as a function of time and distance from the evaporating surface

Day	Hour of day	Tensiometer Readings (cm Hg at porous cups at given dist. from evaporating surface) 2 cm	4 cm	8 cm	12 cm	16 cm	24 cm	30 cm
10-17-58	1200	1.2	1.2	1.2	1.2	1.2	1.2	1.2
	1238	1.2	1.2	1.2	1.2	1.1	1.1	1.0
	1401	1.6	1.5	1.6	1.3	1.4	1.6	1.5
	1656	2.8	2.6	2.9	2.1	2.4	2.3	1.9
	2300	5.8	5.6	5.5	3.9	4.2	3.6	3.1
10-18-58	0045	6.5	6.4	6.1	4.3	4.5	3.9	3.4
	1030	9.8	9.7	9.2	5.8	5.7	4.7	4.0
	1300	10.4	10.2	9.6	5.9	5.8	4.8	4.1
10-19-58	0206[a]	13.6	13.3	12.7	6.3	6.0	4.8	3.9
	1836	12.5	12.3	11.5	4.5	4.5	3.5	2.9
	2345	14.2	13.8	13.1	5.1	4.9	3.8	3.2
10-20-58	0949	16.8	16.5	15.7	5.6	5.5	4.6	3.9
	1536	18.8	18.4	17.5	6.0	5.8	4.8	4.2
	2300	21.1	20.5	19.5	6.2	5.9	5.0	4.3
10-21-58	0830	24.0	23.3	22.1	6.6	6.4	5.4	4.7
	1400	25.8	24.8	23.4	6.5	6.3	5.2	4.7
	1939	27.5	26.3	24.6	6.4	6.2	5.1	4.5
10-22-58	0836	32.3	30.3	27.8	6.3	6.0	5.1	4.5
	1424	34.7	32.4	29.3	6.1	5.8	4.9	4.3
10-23-58	0000	39.3	36.1	31.9	5.8	5.7	4.7	4.2
	1000	45.1	40.7	34.9	4.8	4.7	3.9	3.3
	1700	48.9	43.5	36.8	4.7	4.1	4.3	2.8
10-24-58	1000	56.0	50.8	43.0	4.7	4.6	3.8	3.2
	1700	56.9	52.8	45.5	4.7	4.5	3.7	3.2
10-25-58	1115		55.7	51.5	4.6	4.4	3.6	3.1
	1500		55.8	52.7	4.4	4.0	4.2	2.6

[a]There was no suction on the water reservoir for a period of 20 minutes beginning at this time. Note the interruption in the development of the suction pattern as indicated by the tensiometer readings at the 1836 hour.

Table 14. Run 5A. The distribution of temperature in the soil column as a function of time and distance from the evaporating surface.

Day	0.5 cm Hour	0.5 cm Temp. (°C)	5.0 cm Hour	5.0 cm Temp. (°C)	10.0 cm Hour	10.0 cm Temp. (°C)	16.0 cm Hour	16.0 cm Temp. (°C)	24.0 cm Hour	24.0 cm Temp. (°C)
10-17-58	1144	24.9	1147	24.9	1148	24.9	1149	24.9	1149	24.9
	1201	24.1								
	1202	23.4								
	1203	23.0								
	1204	22.5								
	1236	19.8	1236	23.9	1237	24.8	1237	24.8	1238	24.9
	1404	19.1	1405	23.3	1406	24.4	1407	24.9	1408	24.9
	2302	19.1	2302	23.0	2304	24.3	2305	24.8	2306	24.8
10-18-58	1026	19.3	1027	23.0	1027	24.3	1028	24.8	1028	24.8
10-19-58	0207	19.4	0210	23.0	0211	24.2	0211	24.8	0211	24.8
	1842	19.5	1843	23.0	1844	24.2	1845	24.8	1846	24.8
10-20-58	0953	19.5	0954	23.0	0954	24.2	0955	24.8	0956	24.8
	1540	19.5	1541	23.0	1542	24.2	1543	24.8	1544	24.8
	2303	19.5	2304	23.0	2305	24.2	2305	24.8	2306	24.8
10-21-58	0828	19.5	0828	23.0	0829	24.2	0829	24.8	0832	24.8
	1403	19.3	1404	23.0	1405	24.2	1405	24.8	1406	24.8
	1941	19.3	1942	23.0	1942	24.2	1943	24.8	1944	24.8
10-22-58	0839	19.3	0839	23.0	0840	24.2	0841	24.8	0841	24.8
	1423	19.4	1423	23.0	1424	24.2	1426	24.7	1427	24.8
10-23-58	0003	19.4	0004	22.9	0005	24.1	0006	24.7	0007	24.8
10-24-58	1009	19.5	1010	23.0	1011	24.2	1012	24.8	1013	24.8
10-25-58	1117	19.4	1118	23.0	1119	24.2	1120	24.8	1120	24.8
	1453	19.4	1453	23.0	1454	24.2	1455	24.7	1456	24.8
The flow of air was stopped at 1500 and the return of the sample to temperature equilibrium with the bath was followed. The results follow:										
	1525	23.0								
	1540	23.8	1541	24.0	1541	24.4	1554	24.8	1555	24.9
	1556	24.2	1557	24.4	1558	24.5	1559	24.8	1600	24.9
	1644	24.7	1645	24.8	1646	24.7	1646	24.8	1647	24.9
	1737	24.8	1738	24.9	1738	24.8	1739	24.8	1734	24.8
10-26-58	1415	24.9	1416	25.0	1416	24.9	1417	24.9	1417	25.0

Table 15. Run 6A. Basic data on the evaporation of water from the soil column and its replenishment from the "water table."

Day	Hour of day	Time since last reading Δt (hrs)	Time since expt. began (hrs)	Water evaporated ΔQ (gms)	Rate of evaporation $\Delta Q/\Delta t$ (gm/hr)	Running total of evap., Q (gms)	H_2O uptake from reservoir (cc)	Rate of H_2O uptake by sample (cc/hr)	Running total of uptake (cc)
11- 4-58	1208		.64	4.10	6.41	4.10			
	1330	1.36	2.00	4.27	3.19	8.37			
	1530	2.00	4.00	6.70	3.35	15.07			
	2200	6.50	10.50	19.23	2.96	34.30			
11- 5-58	0150	3.84	14.34	10.15	2.64	44.45			
	0850	7.01	21.35	16.85	2.40	61.30			
	1641	7.83	29.18	17.63	2.25	78.93			
	2006	3.42	32.60	7.53	2.20	86.46			
11- 6-58	0000	3.90	36.50	8.21	2.10	94.67			
	1021	10.35	46.85	20.50	1.98	115.17			
	1700	6.65	53.50	11.01	1.66	126.18			
	2350	6.84	60.34	10.58	1.55	136.76	- 7.0[a]	- .12	- 7.0
11- 7-58	0845	8.91	69.25	12.58	1.41	149.34			
	1630	7.75	77.00	8.64	1.11	157.98			
11- 8-58	1000	17.50	94.50	13.42	0.77	171.40			
	1700	7.00	101.50	3.68	0.53	175.08			
11- 9-58	0000	7.00	108.50	5.78	0.82	180.86			
	1330	13.50	122.00	14.97	1.11	195.83			
	2315	9.75	131.75	9.28	0.95	205.11			
11-10-58	0841	9.43	141.18	9.32	0.99	214.43			
	1700	8.32	149.50	7.56	0.91	221.99			
	2330	6.50	156.00	5.53	0.85	227.52			
11-11-58	0851	9.35	165.35	7.32	0.78	234.84			
	1130						-85.0	- .79	-92.0

[a]See footnote accompanying the basic evaporation data of Run 5A which also applies here.

Table 16. Run 6A. The distribution of moisture in the soil column as a function of time and distance from the evaporating surface.

Tensiometer Readings

Day	Hour of day	(cm Hg at porous cups at given dist. from evaporating surface) 4 cm	8 cm	12 cm	16 cm	24 cm	30 cm
11- 4-58	1100	3.1	3.1	3.1	3.1	3.1	3.1
	1145	3.5	3.5	3.2	3.2	3.4	3.3
	1330	6.5	6.1	4.1	4.0	4.0	3.6
	1530	11.5	10.8	5.8	5.6	5.3	4.7
	2200	22.9	20.3	6.4	6.2	5.7	5.2
11- 5-58	0150	29.2	24.6	6.5	6.3	5.9	5.3
	0850	41.2	32.3	6.5	6.3	5.9	4.9
	1409	49.5	39.1	6.5	6.2	5.8	5.4
	1641	52.0	42.2	6.4	6.3	5.9	5.5
	2006	54.9	46.5	6.4	6.3	5.9	5.4
11- 6-58	0000	54.8	50.3	6.2	6.0	5.6	5.3
	1021	55.4	55.0	5.8	5.6	5.4	5.0
	1700	55.2	55.4	5.1	4.7	5.5	4.1
	2350	54.8	55.4	4.1	3.8	3.6	3.2
11- 7-58	0845		55.8	5.8	5.9	5.7	5.4
	1630			6.0	6.0	5.9	5.6
11- 8-58	1000			5.3	5.2	4.5	3.6
	1700			5.1	5.2	5.1	4.8
11- 9-58	0000			5.2	5.3	5.2	4.9
	1330			5.3	5.3	5.3	5.0
	2315			4.7	4.4	3.5	2.6
11-10-58	0841			4.5	4.4	4.2	3.5
	1700			4.7	4.7	4.0	3.3
	2330			4.8	4.9	5.0	4.6
11-11-58	0851			5.2	5.3	5.3	5.0
	1130			5.3	5.4	5.3	5.1

Table 17. Run 6A. The distribution of temperature in the soil column as a function of time and distance from the evaporating surface.

Day	0.5 cm		5.0 cm		10.0 cm		16.0 cm		24.0 cm	
	Hour	Temp. (°C)	Hour	Temp. (°C)	Hour	Temp. (°C)	Hour	Temp. (°C)	Hour	Temp. (°C)
11-4-58	1100	34.9	1059	34.9	1058	34.9	1058	34.9	1057	34.9
	1103	34.9	1104	34.9						
	1131	32.6								
	1133	30.6	1135	34.9						
	1136	29.1								
	1138	28.3	1141	34.7						
	1143	27.1	1151	34.1	1152	34.9	1152	34.9	1153	34.9
	1148	26.7								
	1154	26.2	1156	33.8						
	1159	25.9	1200	33.7						
	1210	25.6	1209	33.3						
	1242	25.2	1243	32.6	1244	34.5	1245	34.9	1246	34.9
	1328	25.0	1329	32.2	1330	34.3	1332	34.8	1333	34.9
	1533	25.1	1534	31.8	1535	34.1	1536	34.8	1536	34.9
	2204	25.1	2205	31.9	2205	34.1	2207	34.5	2207	34.9
11-5-58	0959	25.3	1000	31.9	1000	34.1	1001	34.8	1002	34.9
	1405	25.2	1406	31.9	1408	33.9	1409	34.6	1409	34.9
	1644	25.6	1645	31.9	1646	34.0	1646	34.7	1647	34.9
	2005	25.2	2008	31.9	2008	34.1	2009	34.8	2010	34.9
	2357	25.7	2358	32.1	2358	33.9	2359	34.8	0000	34.9
11-6-58	1659	27.5	1700	32.4	1701	34.1	1702	34.7	1703	34.8
	2334	28.9	2335	32.7	2336	34.3	2336	34.7	2337	34.8
11-7-58	0838	29.8	0839	32.9	0840	34.3	0841	34.7	0842	34.9
	1633	31.1	1633	33.2	1634	34.3	1634	34.8	1635	34.9
11-8-58	1025	33.1	1026	33.7	1027	34.6	1027	34.8	1028	34.9
	1656	33.3	1657	33.7	1657	34.6	1657	34.8	1658	34.9
11-9-58	0004	29.6	0004	32.8	0003	34.3	0002	34.8	0001	34.9
	1322	31.3	1322	33.0	1324	34.2	1324	34.8	1325	34.9
	2302	31.1	2303	33.3	2304	34.4	2305	34.8	2305	34.9
	0841	31.6	0850	33.2	0850	34.4	0851	34.8	0852	34.9
	1659	31.8	1659	33.3	1700	34.5	1701	34.8	1702	34.9
	2323	32.0	2324	33.3	2324	34.4	2325	34.6	2326	34.9
	0848	32.4	0849	33.4	0850	34.3	0850	34.7	0851	34.9

Table 18. Run 8A. Basic data on the evaporation of water from soil column and its replenishment from the "water table."

Day	Hour of day	Time since last reading Δt (hrs)	Time since expt. began (hrs)	Water evaporated ΔQ (gms)	Rate of evaporation $\Delta Q/\Delta t$ (gm/hr)	Running total of evap., Q (gms)	H_2O uptake from reservoir (cc)	Rate of H_2O uptake by sample (cc/hr)	Running total of uptake (cc)
2-3-59	1500	1.00	1.00	3.50	3.50	3.50			
	1700	2.00	3.00	6.15	3.08	9.65			
	2175	4.75	7.75	13.16	2.77	22.81			
2-4-59	0330	5.75	13.50	15.78	2.74	38.59			
	0340						15	1.11	15
	1210	8.66	22.16	20.95	2.42	59.54			
	1700	4.84	27.00	11.50	2.38	71.04			
2-5-59	0106	8.10	35.10	19.28	2.38	90.32			
	0112						80	3.71	95
	1003	8.95	44.05	20.50	2.29	110.82			
	1445	4.70	48.75	10.90	2.32	121.72			
	2206	7.35	56.10	15.81	2.15	137.53	60	2.86	155
2-6-59	0915	11.15	67.25	23.40	2.10	160.93			
	1600	6.75	74.00	14.05	2.08	174.98			
2-7-59	0224	10.40	84.40	19.90	1.91	194.88			
	1145	9.35	93.75	17.03	1.82	211.91	51	1.36	206

Table 19. Run 8A. The distribution of moisture in the soil column as a function of time and distance from the evaporating surface.

Day	Hour of day	Tensiometer Readings (cm Hg at porous cups at given dist. from evaporating surface) 2 cm	4 cm	8 cm	12 cm	16 cm	24 cm	32 cm
2-3-59	1315	4.1	4.1	4.1	4.1	4.1	4.1	4.1
	1415	4.9	4.5	4.2	4.0	3.9	3.5	3.7
	1436	5.4	4.8	4.5	4.1	4.0	3.6	3.7
	1500	6.1	5.4	5.1	4.7	4.4	4.0	3.9
	1530	6.8	6.0	5.6	5.2	4.8	4.3	4.1
	1700	8.7	7.4	6.8	6.3	5.7	5.0	4.4
	2175	11.7	9.5	8.7	7.9	7.0	5.6	4.9
2-4-59	0330	14.6	11.4	10.2	9.2	7.8	5.9	5.1
	1210	17.9	13.0	11.5	10.2	8.2	6.1	5.1
	1700	18.8	13.6	11.7	10.4	8.1	5.7	4.9
2-5-59	0106	20.2	14.8	12.4	11.4	8.1	5.7	5.0
	1003	23.5	17.6	14.5	12.6	8.9	6.4	5.6
	1445	24.9	19.0	15.4	13.3	9.3	7.0	6.0
	2206	28.6	22.1	16.9	14.1	9.5	7.0	6.0
2-6-59	0915	35.2	27.0	18.7	15.1	9.5	6.8	5.9
	1600	38.4	29.5	19.4	15.1	9.4	6.7	5.7
2-7-59	0224	43.5	34.2	20.9	16.0	9.3	6.8	5.8
	1145	47.3	38.7	22.2	16.6	9.4	6.8	5.9

Table 20. Run 8A. The distribution of temperature in the soil column as a function of time and distance from the evaporating surface.

Day	0.5 cm		5.0 cm		16 cm		24 cm	
	Hour	Temp. (°C)	Hour	Temp. (°C)	Hour	Temp. (°C)	Hour	Temp. (°C)
2-3-59	1310	34.9	1312	35.0	1313	34.9	1313	35.6
	1400	34.9	1400	35.0	1354	34.7	1358	35.5
	1401	33.8						
	1402	32.8						
	1403	32.2	1404	35.0				
	1405	31.1						
	1407	30.4						
	1410	29.5						
	1412	29.0	1413	34.5	1414	34.7	1415	35.4
	1416	28.4	1418	34.1				
	1423	27.5	1421	33.8	1424	34.8	1427	35.3
	1429	27.0	1431	33.0	1433	34.8		
	1434	26.8						
	1446	26.2	1447	32.2	1448	34.8	1451	35.2
	1458	26.0	1502	31.8	1506	34.9	1456	35.2
	1508	26.1	1510	31.6	1512	34.9		
	1522	26.1	1523	31.5	1524	34.9	1526	35.4
	1709	25.9	1711	31.1	1712	34.8		
	2143	25.7	2143	30.9	2145	34.6	2148	35.4
2-4-59	0336	25.4	0336	30.5	0337	34.7	0342	35.2
	1704	25.1	1705	30.1	1705	34.6	1706	35.0
2-5-59	0111	25.0	0110	30.2	0109	34.6	0105	34.9
	1012	25.0	1013	29.9	1013	34.5	1015	34.8
	1448	24.9	1448	30.0	1447	34.5	1444	34.8
	2206	24.7	2207	29.8	2207	34.4	2208	34.7
2-6-59	0922	24.3	0922	29.7	0921	34.2	0920	34.5
	1604	24.6	1605	30.0	1606	34.4	1607	34.7
2-7-59	0230	24.2	0229	29.7	0228	34.4	0227	34.7
	1141	24.2	1142	29.5	1143	34.4	1144	34.6

Table 21. Run 9A. Basic data on evaporation of water from the soil column and its replenishment from the "water table."

Day	Hour of day	Time since last reading Δt (hrs)	Time since expt. began (hrs)	Water evaporated ΔQ (gms)	Rate of evaporation $\Delta Q/\Delta t$ (gm/hr)	Running total of evap., Q (gms)	H_2O uptake from reservoir (cc)	Rate of H_2O uptake by sample (cc/hr)	Running total of uptake (cc)
3-14-59	1200		0.00						
	1245	0.75	0.75	2.25	3.00	2.25			
	1430	1.75	2.50	4.77	2.72	7.02			
	1800	3.50	6.00	8.90	2.54	15.92			
	2130	3.50	9.50	8.23	2.35	24.15	7.5	0.79	7.5
3-15-59	0054	3.40	12.90	7.83	2.30	31.98			
	1418	13.40	26.30	29.45	2.20	61.43			
3-16-59	0000	9.70	36.00	18.60	1.92	80.03	40.0	1.51	47.5
	0845	8.75	44.75	14.93	1.71	94.96	9.5	1.09	57.0
	1700	8.25	53.00	14.08	1.71	109.04			
3-17-59	0000	7.00	60.00	10.95	1.56	119.99	10.0	0.66	67.0
	0800	8.00	68.00	11.62	1.45	131.61	8.0	1.00	75.0
	1730	9.50	77.50	13.10	1.38	144.71	11.0	1.16	86.0
3-18-59	0115	7.75	85.25	9.93	1.28	154.64	9.5	1.22	95.5
	0854	7.65	92.90	8.00	1.05	162.64	8.0	1.04	103.5
	1700	8.10	101.00	8.00	0.99	170.64			
	2345[a]	6.75	107.75	6.42	0.95	177.06	18.0	1.21	121.5
3-19-59	0940	9.92	117.67				10.5	1.06	132.0
	2324	13.73	131.40	10.68	0.78	187.74	12.0	0.87	144.0
3-20-59	0918	9.90	141.30	8.98	0.90	196.64	10.0	1.01	154.0
	1715	7.95	149.25	7.26	0.92	203.90			
3-21-59	0045	7.50	156.75	6.60	0.88	209.50			
	0924	8.65	165.40	7.45	0.86	217.95	25.0	1.04	179.0
3-22-59	0030	15.10	180.50	14.05	0.93	232.00	12.0	0.79	191.0
	1215	11.75	192.25	10.58	0.90	242.58	11.0	0.94	202.0
	2309	10.90	203.15	8.56	0.78	251.14	13.0	1.19	215.0

3-23-59	0815	9.05	212.20	6.83	0.75	257.97	7.5	0.83	222.5
	1724	9.20	221.40	6.95	0.76	264.92	9.0	0.98	231.5
3-24-59	0009	6.75	228.15	4.92	0.73	269.84	6.5	0.96	238.0
	0909	9.00	237.15	6.05	0.67	275.89	9.0	1.00	247.0
	1730	8.35	245.50	5.64	0.68	281.53			
3-25-59	0012	6.70	252.20	4.43	0.66	285.96	14.0	0.93	261.0
	0906	8.90	261.10	5.97	0.67	291.93	7.0	0.79	268.0
	2330	14.40	275.50	8.90	0.62	300.83	12.5	0.87	280.5
3-26-59	0906	9.60	285.10	5.98	0.62	306.81			
	1709	8.05	293.15	4.76	0.59	311.57	17.0	0.96	297.5
	2330	6.35	299.50	3.75	0.59	315.32	4.5	0.71	302.0
3-27-59	0912	9.70	309.20	5.75	0.59	321.07	9.0	0.93	311.0
	2309	13.95	323.15	7.90	0.57	328.97	7.0	0.50	318.0
3-28-59	1100	11.85	335.00	6.20	0.52	335.17			
	2254	11.90	346.90	6.50	0.54	341.67	13.5	0.57	331.5
3-29-59	1245	13.85	360.75	7.31	0.57	348.98	12.0	0.93	343.5
3-30-59	0000	11.25	372.00	5.96	0.53	354.94	8.0	0.71	351.5
	0900	9.00	381.00	4.50	0.50	359.44			
	2245	13.75	394.75	7.11	0.52	366.55	19.0	0.84	370.5
3-31-59	0930	10.75	405.50	5.48	0.51	372.03	8.0	0.74	378.5
	1700	7.50	413.00	3.85	0.51	375.88	4.5	0.60	383.0
4- 1-59	0030	7.50	420.50	3.81	0.51	379.69	3.0	0.40	386.0
	0900	8.50	429.00	4.12	0.48	383.81	6.5	0.77	392.5
4- 2-59	0039	15.65	444.65	7.55	0.48	391.36	9.0	0.57	401.5
	0930	8.85	453.50	4.38	0.50	395.74	8.0	0.89	409.5

[a]While making the reading at this time the hose of the air line became detached and remained off for 10 hours. Note the effect on the moisture and temperature distributions and on the evaporation rate.

Table 22. Run 9A. The distribution of moisture in the soil column as a function of time and distance from the evaporating surface.

Tensiometer Readings

Day	Hour of day	(cm Hg at porous cups at given dist. from evaporating surface) 2 cm	4 cm	8 cm	12 cm	16 cm	24 cm	30 cm
3-14-59	0915	4.6	4.6	4.6	4.6	4.6	4.6	4.6
	1154	4.6	4.6	4.6	4.5	4.7	4.8	4.7
	1230	5.6	5.2	5.0	4.8	4.7	4.5	4.6
	1300	6.4	5.8	5.7	5.2	4.9	4.6	4.7
	1330	7.0	6.3	6.1	5.7	5.3	4.9	4.8
	1430	8.2	7.6	7.2	6.7	6.1	5.6	5.2
	1800	11.4	10.6	9.9	9.2	8.2	7.1	6.5
	2130	14.0	13.0	12.1	11.0	9.6	8.1	7.5
3-15-59	0054	16.2	15.0	13.5	12.2	10.5	8.6	8.1
	1418	28.3	23.0	18.0	15.2	12.2	9.5	9.0
3-16-59	0000	41.2	29.3	20.5	16.7	12.7	9.9	9.3
	0845	53.1	35.2	23.0	18.2	13.5	10.5	9.9
	1700	56.3	39.4	25.0	19.5	14.0	10.9	10.4
3-17-59	0000	56.8	41.5	25.9	19.9	13.8	10.4	9.8
	0800	56.8[a]	43.2	27.1	20.6	14.2	10.7	10.2
	1730		44.3	27.9	21.0	14.2	10.6	10.1
3-18-59	0115		44.4	28.6	21.3	14.1	10.4	10.0
	0854		47.0	29.4	21.7	14.3	10.4	10.0
	1700		47.7	29.9	22.0	14.3	10.4	9.9
	2345		43.3	30.4	22.5	14.6	10.6	10.1
3-19-59	0940		43.8	25.6	19.9	13.4	10.0	9.9
	2324		43.9	28.0	20.9	13.8	10.2	9.7
3-20-59	0918		46.5	30.2	22.8	14.9	15.9	10.4
	1715		47.4	31.6	23.6	15.0	10.9	10.5
3-21-59	0045		48.3	32.4	24.1	15.2	10.9	10.5
	0924		48.8	32.9	24.4	15.2	10.8	10.4
3-22-59	0030		49.1	33.5	24.7	15.1	10.6	10.3
	1215		49.3	33.7	24.6	14.8	10.3	12.7
	2309		49.5	34.1	24.6	14.7	10.1	9.7
3-23-59	0815		49.9	34.5	24.6	14.8	10.3	9.7
	1724		49.9[a]	34.9	24.8	14.9	10.4	9.7
3-24-59	0009			35.8	25.3	15.0	10.3	9.7
	0909			36.5	25.9	15.2	10.5	9.8
	1730			36.9	26.2	15.1	10.3	9.8
3-25-59	0012			37.3	26.5	15.3	10.6	10.0
	0906			37.9	27.0	15.6	10.9	10.4
	2330			38.9	27.8	15.8	11.0	10.4
3-26-59	0906			39.3	28.2	15.8	10.9	10.5
	1709			39.7	28.3	15.7	10.9	10.3
	2330			40.0	28.3	15.7	10.9	10.3
3-27-59	0912			40.4	28.5	15.6	10.9	10.3
	2309			41.0	28.7	15.7	10.8	10.2
3-28-59	1100			41.6	29.1	15.7	10.8	10.3
	2254			41.6	29.2	15.4	10.4	10.0

[a]Water column of tensiometer has broken.

Table 22. Continued.

Tensiometer Readings

Day	Hour of day	(cm Hg at porous cups at given dist. from evaporating surface) 2 cm	4 cm	8 cm	12 cm	16 cm	24 cm	30 cm
3-29-59	1245			42.1	29.5	15.3	10.1	9.7
3-30-59	0000			42.1	29.6	15.3	10.3	9.8
	0900			42.2	29.6	15.2	10.1	9.7
	2245			42.7	29.8	14.9	9.8	9.4
3-31-59	0930			43.3	30.3	15.3	10.5	9.9
	1700			43.5	30.5	15.4	10.6	10.1
4- 1-59	0030			43.9	30.8	15.5	10.7	10.1
	0900			44.2	31.2	15.6	10.7	10.3
4- 2-59	0039			44.6	31.7	15.6	10.6	10.2
	0930			44.9	31.8	15.5	10.6	10.2

Table 23. Run 9A. The distribution of temperature in the soil column as a function of time and distance from the evaporating surface.

Day	0.5 cm		5.0 cm		16 cm		24 cm	
	Hour	Temp. (°C)	Hour	Temp. (°C)	Hour	Temp. (°C)	Hour	Temp. (°C)
3-11-59	0958	29.1	0957	29.1	0955	29.1	0954	29.1
3-13-59	1014	29.1	1015	29.1	1017	29.1	1020	29.1
3-14-59	0920	29.1	0919	29.1	0918	29.1	0917	29.1
	1158	29.1	1200	29.1				
	1201	28.5						
	1202	28.0			1203	29.1		
	1206	25.7	1207	29.1				
	1212	24.4	1215	28.9				
	1217	23.4			1218	29.1	1220	29.1
	1225	22.8	1226	28.3	1227	29.1		
	1232	22.5	1233	28.0				
	1236	22.2	1235	27.9				
	1243	22.1	1245	27.6	1248	39.1	1250	29.1
	1254	21.8	1255	27.4				
	1306	21.7	1307	27.2	1308	29.2	1310	29.1
	1314	21.6	1315	27.3				
	1334	21.5	1335	26.9	1336	29.1	1339	29.1
	1345	21.4	1347	26.9	1347	29.1		
	1438	21.4	1439	26.7	1439	29.1	1441	29.1
	1803	21.4	1803	26.6	1802	29.0	1801	29.1
	2134	21.4	2135	26.6	2136	29.0	2137	29.0
3-15-59	0057	21.5	0055	26.6	0054	29.0	0053	29.1
	1419	21.6	1420	26.6	1421	28.9	1426	28.9
3-16-59	0014	21.7	0013	26.7	0012	28.9	0011	29.0
	0844	21.9	0847	26.7	0848	28.8	0850	28.9
	1712	22.3	1709	26.9	1708	28.9	1705	29.0
3-17-59	0006	22.6	0007	27.0	0009	28.9	0010	29.0
	0803	22.8	0802	27.0	0801	28.9	0800	29.1
	1728	23.1	1729	27.1	1730	28.9	1732	29.0
3-18-59	0111	23.6	0112	27.3	0114	28.9	0116	28.9
	0855	24.0	0854	27.4	0853	28.9	0851	29.0
	1659	24.2	1700	27.5	1701	28.9	1703	29.0
	2347	24.2	2346	27.5	2346	28.9	2345	28.8
3-19-59	2315	24.0	2314	27.3	2313	28.8	2312	28.8
3-20-59	0907	24.5	0907	27.5	0908	28.9	0910	29.0
	1719	24.5	1718	27.6	1717	28.9	1716	29.0
3-21-59	0041	24.6	0042	27.6	0043	28.9	0044	29.0
	0925	24.7	0923	27.6	0923	28.9	0922	28.8
3-22-59	1210	24.0	1210	27.6	1211	28.9	1211	29.0
	2309	24.9	2308	27.6	2308	28.8	2307	28.8
3-23-59	1721	25.0	1720	27.6	1719	28.9	1718	28.8
3-24-59	0005	25.0	0006	27.7	0007	28.9	0008	28.9
	0910	25.2	0909	27.6	0908	28.8	0907	28.7
	1724	25.3	1725	27.7	1726	28.9	1728	28.9

Table 23. Continued.

Day	0.5 cm		5.0 cm		16 cm		24 cm	
	Hour	Temp. (°C)	Hour	Temp. (°C)	Hour	Temp. (°C)	Hour	Temp. (°C)
3-25-59	0011	25.4	0010	27.7	0010	28.9	0009	28.9
	0905	25.5	0905	27.7	0906	28.9	0909	28.9
	2336	25.4	2335	27.7	2334	28.9	2333	28.8
3-26-59	0902	25.6	0902	27.7	0904	28.9	0905	29.0
	1710	25.3	1708	27.7	1708	28.9	1707	28.9
	2331	25.5	2332	27.7	2333	28.8	2334	28.8
3-27-59	0910	25.5	0909	27.7	0908	28.9	0907	28.8
3-28-59	1107	25.4	1105	27.7	1104	28.9	1102	28.8
	2247	25.9	2247	27.7	2248	28.9	2249	28.8
3-30-59	2359	25.9	2359	27.7	0000	28.7	0002	28.6
	0908	25.9	0907	27.8	0906	28.9	0905	28.9
	2239	25.9	2239	27.7	2240	28.8	2242	28.7
3-31-59	0935	25.9	0934	27.7	0933	28.8	0932	28.7
	1659	26.0	1659	27.8	1701	28.8	1702	28.8
4- 1-59	0033	26.0	0032	27.8	0032	28.9	0030	28.8
	0905	26.0	0905	27.8	0907	28.9	0910	28.8
4- 2-59	0044	25.9	0039	27.7	0038	28.8	0938	28.6
	0931	26.0	0932	27.7	0932	28.8	0933	28.7

Table 24. Run 11A. Basic data on the evaporation of water from the soil column and its replenishment from the "water table."

Day	Hour of day	Time since last reading Δt (hrs)	Time since expt. began (hrs)	Water evaporated ΔQ (gms)	Rate of evaporation $\Delta Q / \Delta t$ (gm/hr)	Running total of evap., Q (gms)	H_2O uptake from reservoir (cc)	Rate of H_2O uptake by sample (cc/hr)	Running total of uptake (cc)
4-17-59	1145		.75	2.15	2.87	2.15			
	1245	1.00	1.75	2.31	2.31	4.46	0.0	0.00	
	1415	1.50	3.25	2.89	1.93	7.35			
	1700	2.75	6.00	5.18	1.88	12.53	2.0	0.47	2.0
	2000	3.00	9.00	5.70	1.90	18.23	3.5	0.53	5.5
	2339	3.65	12.65	6.52	1.79	24.75			
4-18-59	0930	9.85	22.50	17.27	1.75	42.02	6.0	0.61	11.5
	1339	4.15	26.65	6.27	1.51	48.29			
	2030	6.85	33.50	12.10	1.76	60.39	10.0	0.91	21.5
4-19-59	0136	4.90	38.50	8.20	1.67	68.59	2.5	0.51	24.0
	0845	7.35	45.75	11.03	1.50	79.62	1.0	0.14	25.0
	1215	3.50	49.25	5.60	1.60	85.22	3.0	0.86	28.0
	1700	4.75	54.00	7.35	1.55	92.57	4.0	0.84	32.0
	2130	4.50	58.50	6.50	1.44	99.07	4.0	0.89	36.0
4-20-59	0106	3.60	62.10	5.03	1.40	104.10			
	0754	6.80	68.90	8.61	1.27	112.71			
	1200	4.10	73.00	4.93	1.20	117.64	10.5	0.96	46.5
	1612	4.20	77.20	4.87	1.16	122.51	3.0	0.71	49.5
	2036	4.40	81.60	4.82	1.10	127.33	4.5	1.02	53.0
4-21-59	0024	3.80	85.40	4.15	1.09	131.48	6.0	1.58	59.0
	0915	8.85	94.25	9.20	1.04	140.68	6.0	0.68	65.0
	1200	2.75	97.00	2.96	1.08	143.64	4.0	1.45	69.0
	1554	3.90	100.90	3.40	0.87	147.04	4.5	1.15	73.5

Table 25. Run 11A. The distribution of moisture in the soil column as a function of time and distance from the evaporating surface.

Day	Hour of day	Tensiometer Readings (cm Hg at porous cups at given dist. from evaporating surface) 2 cm	4 cm	8 cm	12 cm	16 cm	24 cm	30 cm
4-17-59	1056	4.2	4.2	4.0	4.2	4.1	4.1	4.4
	1115	4.3	4.2	4.0	4.1	3.9	3.9	4.3
	1130	4.5	4.4	4.1	4.2	3.9	3.8	4.2
	1145	4.7	4.5	4.2	4.2	3.9	3.9	4.2
	1226	5.3	4.9	4.6	4.6	4.2	4.1	4.3
	1245	5.6	5.2	4.8	4.8	4.4	4.3	4.4
	1415	6.9	6.3	5.7	5.7	5.0	4.7	4.6
	1700	9.1	8.1	7.3	7.2	6.2	5.7	5.3
	2000	11.2	10.0	8.8	8.5	7.2	6.4	5.9
	2339	13.4	11.9	10.2	9.6	8.1	6.9	6.4
4-18-59	0930	20.1	17.0	13.6	12.4	10.1	8.2	7.7
	1339	23.0	18.9	14.6	13.2	10.5	8.3	7.8
	2030	29.7	23.0	16.7	14.9	11.8	9.1	8.6
4-19-59	0136	34.9	25.8	17.9	15.8	12.3	9.2	8.7
	0845	43.1	30.0	19.8	17.3	13.2	9.7	9.2
	1215	47.4	32.1	20.7	17.9	13.5	9.7	9.2
	1700	51.6	34.5	21.8	18.6	14.0	10.0	9.4
	2130	55.0	36.7	22.6	19.3	14.4	10.0	9.6
4-20-59	0106	56.8	38.3	23.3	19.7	14.3	9.3	9.1
	0754	58.2	40.8	23.2	20.4	15.0	10.2	9.6
	1200	58.5	42.0	24.8	20.9	15.4	10.4	9.9
	1612	58.6	43.1	25.3	21.2	15.5	10.2	9.7
	2036	58.7	44.1	25.7	21.5	15.7	10.3	9.8
4-21-59	0024	58.7	44.8	26.0	21.5	15.4	9.6	9.3
	0915	58.9	45.9	26.3	21.8	15.7	9.9	9.4
	1200	58.9	46.1	26.4	21.9	15.6	9.6	9.1
	1554		46.4	26.7	22.2	16.0	10.1	9.6

Table 26. Run 11A. The distribution of temperature in the soil column as a function of time and distance from the evaporating surface.

Day	0.5 cm		5.0 cm		16 cm		24 cm	
	Hour	Temp. (°C)	Hour	Temp. (°C)	Hour	Temp. (°C)	Hour	Temp. (°C)
4-17-59	0944	22.3	0945	22.3	0946	22.2	0948	22.2
	1056	22.3	1056	22.3	1055	22.2	1054	22.2
	1101	21.9						
	1102	21.3						
	1104	20.4	1105	22.3				
	1106	19.8						
	1108	19.3						
	1109	19.1	1110	22.2	1112	22.1	1112	22.3
	1113	18.6	1114	22.1				
	1115	18.3	1118	21.9				
	1120	17.8	1122	21.8	1124	22.2		
	1125	17.5	1127	21.7	1130	22.2		
	1128	17.4						
	1134	17.2	1135	21.4			1133	22.2
	1137	17.1	1141	21.3				
	1145	17.0	1144	21.2	1143	22.2		
	1152	16.8	1153	21.1	1154	22.2	1155	22.2
	1205	16.8	1206	20.9	1207	22.2	1208	22.2
	1225	16.6	1223	20.5	1222	22.2	1220	22.3
	1242	16.5	1243	20.7	1244	22.2	1244	22.3
	1305	16.6	1303	20.7	1303	22.2	1302	22.3
	1416	16.4	1418	20.7	1419	22.2	1420	22.3
	1700	16.7	1701	20.7	1659	22.2	1658	22.3
	2005	16.8	2006	20.7	2006	22.2	2007	22.3
	2338	16.8	2337	20.7	2336	22.2	2336	22.3
4-18-59	0926	17.0	0927	20.8	0928	22.2	0929	22.3
	1310	17.1	1309	20.8	1308	22.2	1307	22.3
	2027	17.0	2026	20.8	2026	22.2	2027	22.2
4-19-59	0127	17.3	0128	20.8	0124	22.2	0123	22.3
	0837	17.4	0838	20.9	0838	22.2	0840	22.2
	1220	17.5	1224	20.9	1218	22.2	1217	22.3
	1651	17.8	1652	20.9	1654	22.2	1655	22.3
	2130	17.9	2129	21.0	2129	22.2	2128	22.2
4-20-59	0103	18.2	0104	21.1	0105	22.2	0105	22.3
	0754	18.5	0753	21.1	0752	22.2	0751	22.3
	1158	18.6	1159	21.3	1200	22.3	1201	22.4
	1608	18.8	1606	21.3	1605	22.3	1604	22.4
	2030	19.1	2034	21.3	2033	22.3	2032	22.4
4-21-59	0018	19.5	0019	21.3	0020	22.3	0021	22.4
	0910	19.4	0911	21.3	0912	22.2	0914	22.3
	1159	19.8	1201	21.3	1202	22.3	1203	22.3
	1552	19.9	1551	21.3	1551	22.2	1549	22.2

Table 27. Run 12A. Basic data on the evaporation of water from the soil column and its replenishment from the "water table."

Day	Hour of day	Time since last reading Δt (hrs)	Time since expt. began (hrs)	Water evaporated ΔQ (gm/hr)	Rate of evaporation $\Delta Q/\Delta t$ (gm/hr)	Running total of evap., Q (gms)	H_2O uptake from reservoir (cc)	Rate of H_2O uptake by sample (cc/hr)	Running total of uptake (cc)
4-29-59	1045		.75	3.73	4.97	3.73			
	1130	.75	1.50	2.15	2.87	5.88			
	1236	1.10	2.60	2.32	2.11	8.20			
	1515	2.65	5.25	5.30	2.00	13.50			
	1645	1.50	6.75	2.87	1.91	16.37	.5	.07	.5
	2045	4.00	10.75	6.70	1.68	23.07			
	2330	2.75	13.50	5.10	1.85	28.17	1.0	.15	1.5
4-30-59	0745	8.25	21.75	15.12	1.83	43.29	6.0	.73	7.5
	1200	4.25	26.00	7.53	1.77	50.82			
	1530	3.50	29.50	6.00	1.71	56.82	3.5	.45	11.0
	2100	5.50	35.00	9.32	1.69	66.14	6.0	1.09	17.0
	2330	2.50	37.50	3.20	1.68	70.34			
5- 1-59	0754	8.40	45.90	13.55	1.61	83.89	9.5	.87	26.5
	1200	4.10	50.00	6.44	1.57	90.33			
	1645	4.75	54.75	6.43	1.35	96.76	5.0	.56	31.5
	1839	1.90	56.65	2.58	1.36	99.34			
	2300	4.35	61.00	5.98	1.38	105.32	5.5	.88	37.0
5- 2-59	0300	4.00	65.00	6.05	1.51	111.37	3.5	.88	40.5
	0930	6.50	71.50	10.30	1.58	121.67	5.0	.77	45.5
	1312	3.70	75.20	5.50	1.49	127.17	3.0	.81	48.5
	1730	4.30	79.50	6.58	1.53	133.75			
	2324	5.90	85.40	8.28	1.40	142.03	8.5	.83	57.0
5- 3-59	0854	9.50	94.90	13.38	1.41	155.41	9.0	.95	66.0
	1224	3.50	98.40	4.70	1.34	160.11	2.0	.57	68.0
	1751	5.45	103.85	6.70	1.23	166.81	4.5	.82	72.5
5- 4-59	0103	7.20	111.05	9.80	1.36	176.61	6.0	.83	78.5
	0906	8.05	119.10	10.05	1.25	186.66	7.0	.87	85.5

	1218	3.20	122.30	4.35	1.36	191.01			
	1642	4.40	126.70	5.46	1.24	196.47	7.0	.92	92.5
	2215	5.55	132.25	6.22	1.12	202.69			
5- 5-59	0100	2.75	135.00	2.93	1.06	205.62	7.5	.90	100.0
	0936	8.60	143.60	8.54	.99	214.16	8.0	.93	108.0
	1312	3.60	147.20	3.61	1.00	217.77	4.5	1.25	112.5
	1715	4.05	151.25	4.10	1.01	221.87			
	2145	4.50	155.75	4.20	.93	226.07	6.5	.76	119.0
5- 6-59	0124	3.65	159.40	3.30	.90	229.37			
	0930	8.10	167.50	7.32	.90	236.69	10.2	.87	129.2
	1518	5.80	173.30	5.45	.94	242.14	4.0	.69	133.2
	2130	6.20	179.50	5.52	.89	247.66	3.4	.55	136.6
5- 7-59	0230	5.00	184.50	4.49	.90	252.15	6.2	1.24	142.8
	0924	6.90	191.40	6.20	.90	258.35	5.8	.84	148.6

Table 28. Run 12A. The distribution of moisture in the soil column as a function of time and distance from the evaporating surface.

Tensiometer Readings

Day	Hour of day	(cm Hg at porous cups at given dist. from evaporating surface) 2 cm	4 cm	8 cm	12 cm	16 cm	24 cm	30 cm
4-29-59	0930	4.4	4.5	4.5	4.4	4.6	4.5	4.4
	1033	4.3	4.4	4.5	4.2	4.4	4.5	4.3
	1045	4.4	4.5	4.5	4.3	4.5	4.5	4.3
	1130	5.0	4.8	4.9	4.6	4.6	4.6	4.3
	1236	5.9	5.4	5.6	5.3	5.1	4.6	4.5
	1515	7.7	6.9	7.1	6.7	6.3	5.7	5.2
	1645	8.6	7.8	7.9	7.4	7.0	6.4	5.7
	2045	10.5	9.6	9.3	8.7	8.1	7.3	6.5
	2330	12.9	11.5	10.9	10.2	9.4	8.2	7.4
4-30-59	0745	18.2	16.0	14.1	12.9	11.4	9.5	7.8
	1200	21.2	18.2	15.5	14.0	12.0	9.7	9.0
	1530	23.9	20.0	16.5	14.8	12.5	10.1	9.3
	2100	29.1	23.0	18.2	16.2	12.5	10.8	10.0
	2330	31.7	24.3	18.8	16.6	13.6	10.5	9.7
5- 1-59	0754	41.7	29.3	21.2	18.5	14.9	11.5	10.6
	1200	47.4	31.9	22.3	19.3	15.2	11.4	10.6
	1645	51.4	34.3	23.5	20.1	15.7	11.5	10.7
	1839	52.8	35.2	23.8	20.3	15.7	11.3	10.5
	2300	55.9	37.0	24.6	20.9	15.2	11.8	10.8
5- 2-59	0300	58.0	38.7	25.3	21.4	16.5	12.0	11.0
	0930	59.3	41.1	26.4	22.3	17.1	12.3	11.3
	1312	59.7	42.5	27.1	22.7	17.3	12.4	11.4
	1730	60.0	44.0	27.8	23.3	17.6	12.6	11.5
	2324	60.4	46.4	28.7	24.0	18.1	12.8	11.7
5-3-59	0854	60.5	48.5	30.0	24.9	18.6	12.9	11.9
	1224	60.4	49.3	30.3	25.1	18.6	12.7	11.7
	1751		50.5	30.8	25.5	18.8	12.7	11.7
5- 4-59	0103		51.8	31.5	26.0	19.1	12.9	11.9
	0906		52.8	32.3	26.6	19.6	13.3	12.3
	1218		53.1	32.6	26.8	19.6	13.1	12.2
	1642		54.5	33.2	27.2	19.9	13.3	12.2
	2215		56.1	34.1	27.8	20.2	13.3	12.3
5- 5-59	0100		56.6	34.5	28.0	20.1	12.8	12.0
	0936		57.7	35.2	28.4	20.4	13.0	11.9
	1312		57.9	35.5	28.6	20.4	13.0	11.9
	1715		58.1	35.7	28.7	20.3	12.8	11.7
	2145		58.3	36.0	28.9	20.6	12.8	11.9
5- 6-59	0124		58.4	36.0	28.8	20.2	12.4	11.5
	0930		58.7	36.4	29.3	20.9	13.3	12.2
	1518		58.8	36.6	39.4	20.9	14.0	11.9
	2130		59.0	36.9	29.6	21.1	13.3	12.1
5- 7-59	0230			37.2	29.8	21.3	13.4	12.3
	0924		59.4	37.6	30.2	21.5	13.5	12.4

Table 29. Run 12A. The distribution of temperature in the soil column as a function of time and distance from the evaporating surface.

Day	0.5 cm		5.0 cm		16 cm	
	Hour	Temp. (°C)	Hour	Temp. (°C)	Hour	Temp. (°C)
4-29-59	0935	22.3	0937	22.3	0939	22.3
	1003	22.2				
	1005	22.2				
	1010	22.2	1011	22.3		
	1017	22.1				
	1023	22.2	1024	22.3		
	1029	22.1				
	1031	22.0				
	1036	20.5				
	1038	20.1				
	1040	19.7				
	1042	19.3				
	1044	19.0				
	1048	18.5	1050	21.9	1051	22.3
	1054	18.2				
	1055	18.0	1056	21.8		
	1100	17.7	1058	21.7		
	1101	17.6	1102	21.6		
	1114	17.3	1112	21.4		
	1115	17.2			1117	22.2
	1122	17.1	1124	21.2		
	1126	17.1				
	1140	17.1	1141	21.3	1142	22.3
	1250	16.9	1232	20.9	1233	22.3
	1519	16.7	1520	20.7	1521	22.2
	1638	16.7	1640	20.7	1641	22.2
	2042	16.9	2040	20.7	2039	22.2
	2330	16.6	2334	20.6	2335	22.2
4-30-59	0750	16.6	0751	20.7	0752	22.2
	1205	17.0	1206	20.7	1208	22.2
	1523	17.1	1525	20.7	1526	22.2
	2055	17.0	2056	20.6	2057	22.2
	2321	17.0	2322	20.7	2323	22.2
5- 1-59	0918	17.1	0919	20.7	0920	22.1
	1157	17.6	1158	20.8	1158	22.2
	1640	17.7	1642	20.8	1643	22.2
	2300	17.7	2308	20.9	2310	21.9
5- 2-59	0254	17.6	0256	20.9	0257	22.1
	0933	17.7	0934	20.9	0934	22.2
	1305	18.0	1306	20.9	1307	22.2
	1725	17.6	1727	20.9	1729	22.1
	2317	17.8	2318	20.9	2320	22.1
5- 3-59	0846	17.8	0847	20.9	0848	22.1
	1215	18.1	1216	20.9	1216	22.1
	1720	17.9	1722	20.9	1723	22.1

Table 29. Continued.

Day	0.5 cm		5.0 cm		16 cm	
	Hour	Temp. (°C)	Hour	Temp. (°C)	Hour	Temp. (°C)
5- 4-59	0044	18.0	0045	21.0	0046	22.1
	0912	18.0	0914	21.0	0915	22.1
	1214	18.1	1215	21.0	1216	22.1
	1637	18.3	1638	21.0	1640	22.1
	2204	18.5	2205	21.1	2206	22.1
5- 5-59	0056	18.5	0058	21.1	0058	22.1
	0931	18.6	0932	21.2	0933	22.1
	1306	19.0	1307	21.2	1308	22.1
	1720	19.0	1722	21.2	1723	22.1
	2130	19.0	2131	21.2	2131	22.1
5- 6-59	0121	18.9	0121	21.2	0122	22.1
	0925	19.0	0926	21.2	0927	22.1
	1508	19.1	1509	21.2	1510	22.1
	2125	19.1	2126	21.2	2127	22.1
5- 7-59	0221	19.1	0223	21.2	0224	22.1
	0913	19.0	0914	21.2	0916	22.1

Table 30. Run 13A. Basic data on the evaporation of water from the soil column and its replenishment from the "water table."

Day	Hour of day	Time since last reading Δt (hrs)	Time since expt. began (hrs)	Water evaporated ΔQ (gms)	Rate of evaporation $\Delta Q / \Delta t$ (gm/hr)	Running total of evap., Q (gms)	H_2O uptake from reservoir (cc)	Rate of H_2O uptake by sample (cc/hr)	Running total of uptake (cc)
5-12-59	1045		.75	1.10	1.47	1.10			
	1130	.75	1.50	1.21	1.61	2.31			
	1236	1.10	2.60	1.40	1.27	3.71	-1.0	- .38	- 1.0
	1518	2.70	5.30	3.40	1.26	7.11			
	1700	1.70	7.00	2.06	1.21	9.17	.8	.18	- 0.2
	2045	3.75	10.75	4.51	1.20	13.68	.8	.21	0.6
	2354	3.15	13.90	3.68	1.17	17.36			
5-13-59	0733	7.65	21.55	8.50	1.11	25.86	6.3	.58	6.9
	1200	4.45	26.00	4.78	1.07	30.64			
	1530	3.50	29.50	3.85	1.10	34.49	3.5	.44	10.4
	2100	5.50	35.00	5.64	1.02	40.13	2.0	.36	12.4
	2330	2.50	37.50	2.76	1.10	42.89			
5-14-59	0754	8.40	45.90	8.39	1.00	51.28	9.5	1.13	21.9
	1203	4.15	50.05	4.02	0.97	55.30			
	1645	4.70	54.75	4.63	0.98	59.93	3.4	.38	25.3
	2012	3.45	58.20	3.11	0.90	63.04			
	2300	2.80	61.00	2.63	0.94	65.67	7.3	1.17	32.6
5-15-59	0930	10.50	71.50	9.46	0.90	75.13	6.4	.61	39.0
	1257	3.45	74.95	3.07	0.89	78.20			
	1733	4.60	79.55	4.06	0.88	82.26	6.7	.83	45.7
	2324	5.85	85.40	5.22	0.89	87.48	5.0	.85	50.7
5-16-59	0854	9.50	94.90	8.38	0.88	95.86	7.5	.79	58.2
	1224	3.50	98.40	3.30	0.94	99.16	3.5	1.00	61.7
	1630	4.10	102.50	3.53	0.86	102.69	2.5	.61	64.2
5-17-59	0000	7.50	110.00	6.56	0.87	109.25	6.5	.87	70.7
	0906	9.10	119.10	7.81	0.86	117.06	6.0	.66	76.7
	1218	3.20	122.30	2.76	0.86	119.82	3.0	.94	79.7

	1745	5.45	127.75	4.61	0.84	124.43	3.3	.60	83.0
	2300	5.25	133.00	4.39	0.84	128.82	5.4	1.03	88.4
5-18-59	0936	10.60	143.60	8.29	0.78	137.11	8.6	.81	97.0
	1136	2.00	145.60	1.80	0.90	138.91			
	1715	5.65	151.25	4.41	0.78	143.32			
	2330	6.25	157.50	5.05	0.81	148.37	8.6	.72	105.6
5-19-59	0930	10.00	167.50	7.98	0.80	156.35	6.3	.63	111.9
	1330	4.00	171.50	3.14	0.78	159.49	3.4	.85	115.3
	1715	3.75	175.25	2.86	0.76	162.35	2.0	.53	117.3
	2300	5.75	181.00	4.57	0.79	166.92	5.5	.96	122.8
5-20-59	0915	10.25	191.25	7.56	0.74	174.48	6.0	.58	128.8
	1245	3.50	194.75	2.84	0.81	177.32			
	1715	4.50	199.25	3.56	0.79	180.88	5.2	.65	134.0
5-21-59	0045	7.50	206.75	0.00[a]		180.88	6.8	.91	140.8
	0930	8.75	215.50	7.34	0.84	188.22	3.8	.43	144.6
	1300	3.50	219.00	2.91	0.83	191.13	3.4	.97	148.0
	1700	4.00	223.00	3.00	0.75	194.13	2.8	.70	150.8
	2300	6.00	229.00	4.54	0.76	198.67	3.9	.65	154.7
5-22-59	0915	10.25	239.25	8.00	0.78	206.67	6.2	.60	160.9
	1258	3.72	242.97	2.80	0.75	209.47			
	1700	4.03	247.00	3.10	0.77	212.57	5.8	.75	166.7
	2345	6.75	253.75	4.92	0.73	217.49	3.7	.55	170.4
5-23-59	0933	9.80	263.55	7.31	0.74	224.80	7.1	.72	177.5
	1300	3.45	267.00	2.56	0.74	227.36	4.9	1.42	182.4

[a]Hose of air line became detached so that no air passed by the sample for 7.5 hours. Note that the evaporation rate is hardly affected.

Table 31. Run 13A. The distribution of moisture in the soil column as a function of time and distance from the evaporating surface.

Tensiometer Readings

Day	Hour of day	(cm Hg at porous cups at given dist. from evaporating surface) 2 cm	4 cm	8 cm	12 cm	16 cm	24 cm	30 cm
5-12-59	0958	3.2	3.2	3.2	3.2	3.2	3.2	3.2
	1030	3.3	3.3	3.2	3.2	3.1	3.2	3.2
	1045	3.4	3.4	3.3	3.2	3.2	3.3	3.2
	1130	3.9	3.7	3.6	3.5	3.4	3.5	3.4
	1236	4.5	4.2	4.0	3.9	3.8	3.9	3.5
	1518	5.8	5.4	5.1	4.9	4.7	4.5	4.0
	1700	6.4	5.9	5.6	5.4	5.1	4.9	4.3
	2045	7.6	7.1	6.6	5.3	5.9	5.3	4.9
	2354	8.6	7.9	7.4	7.0	6.4	5.8	5.2
5-13-59	0733	10.9	10.1	9.3	8.6	7.7	6.7	6.1
	1200	12.0	11.1	10.0	9.3	8.1	6.9	6.3
	1530	12.8	11.8	10.6	9.8	8.4	7.0	6.5
	2100	14.0	12.8	11.3	10.3	8.7	7.0	5.1
	2330	14.4	13.2	11.6	10.5	8.7	6.9	5.8
5-14-59	0754	16.1	14.6	12.6	11.4	9.4	7.4	6.8
	1203	16.9	15.2	13.1	11.7	9.4	7.1	6.6
	1645	17.8	16.0	13.5	12.1	9.8	7.5	6.9
	2012	18.3	16.4	13.8	12.3	9.8	7.3	6.7
	2300	18.7	16.7	14.0	12.5	9.9	7.4	6.8
5-15-59	0930	20.2	17.8	14.8	13.1	10.4	7.9	7.1
	1257	20.7	18.2	15.0	13.2	10.4	7.7	7.0
	1733	21.5	18.8	15.4	13.6	10.7	8.0	7.2
	2324	22.4	19.4	15.8	13.9	11.0	8.1	7.3
5-16-59	0854	24.2	20.6	16.7	14.6	11.6	8.7	8.0
	1224	24.8	21.1	16.9	14.8	11.5	8.1	5.4
	1630	25.5	21.5	17.1	14.9	11.4	8.0	6.8
5-17-59	0000	26.6	22.3	17.5	15.1	11.5	8.0	
	0906	27.8	23.0	17.8	15.3	11.5	7.8	6.2
	1218	28.1	23.2	17.9	15.4	11.4	7.6	6.5
	1745	28.6	23.5	18.0	15.5	11.5	7.6	6.7
	2300	29.2	23.9	18.2	15.6	11.6	7.9	7.0
5-18-59	0936	30.4	24.6	18.6	16.0	11.9	8.0	7.2
	1136	30.5	24.8	18.6	15.9	11.5	7.1	6.8
	1715	30.9	25.0	18.7	16.0	11.7	7.7	3.7
	2330	31.8	25.5	19.0	16.2	12.1	8.1	6.7
5-19-59	0930	33.2	26.4	19.5	16.8	12.4	8.2	7.4
	1330	33.4	26.8	19.7	16.9	12.3	8.1	7.3
	1715	34.2	27.1	19.8	17.0	12.4	8.1	7.4
	2300	34.9	27.5	20.1	17.1	12.6	8.3	7.5
5-20-59	0915	35.8	28.2	20.6	17.6	13.0	8.6	8.0
	1245	36.3	28.5	20.7	17.6	12.9	8.4	7.8
	1715	37.2	28.9	20.8	17.7	13.0	8.5	7.8
5-21-59	0045	25.8	24.6	19.5	16.9	12.6	8.5	8.0[a]

[a]Hose of the air line became detached so that no (dry) air passed by the sample for 7.5 hours.

Table 31. Continued.

Day	Hour of day	(cm Hg at porous cups at given dist. from evaporating surface) 2 cm	4 cm	8 cm	12 cm	16 cm	24 cm	30 cm
	0930	31.3	25.0	18.8	16.3	12.3	8.4	7.7
	1300	33.3	26.1	19.3	16.7	12.5	8.3	7.8
	1700	34.8	27.1	19.8	17.1	12.6	8.2	7.6
	2300	36.2	28.2	20.5	17.7	13.0	8.5	7.8
5-22-59	0915	39.1	30.1	21.4	18.5	13.5	8.9	8.2
	1258	39.7	30.6	21.8	18.7	13.6	8.7	8.1
	1700	40.3	31.0	22.1	18.8	13.7	8.9	8.0
	2345	41.1	31.6	22.4	19.0	13.9	8.9	8.1
5-23-59	0933	42.5	32.6	22.9	19.4	14.1	9.0	8.2
	1300	43.0	32.8	22.9	19.4	13.6	8.2	7.8

Table 32. Run 13A. The distribution of temperature in the soil column as a function of time and distance from the evaporating surface.

Day	0.5 cm		5.0 cm		16 cm	
	Hour	Temp. (°C)	Hour	Temp. (°C)	Hour	Temp. (°C)
5-12-59	0941	22.3	0943	22.3	0944	22.3
	0959	22.3				
	1002	21.9				
	1005	21.3				
	1007	21.3				
	1008	21.1				
	1010	20.7	1012	22.3	1014	22.3
	1017	20.4				
	1023	19.9	1025	22.0	1027	22.3
	1030	19.8	1032	22.0		
	1038	19.6	1040	21.9	1041	22.3
	1050	19.3	1052	21.7		
	1105	18.9	1107	21.6	1108	22.3
	1113	19.0	1115	21.5		
	1117	18.9				
	1127	18.7	1128	21.4		
	1146	18.7	1147	21.4	1148	22.3
	1236	18.6	1240	21.3	1241	22.3
	1522	18.6	1523	21.2	1524	22.3
	1658	18.6	1659	21.2	1711	22.3
	2041	18.6	2042	21.2	2043	22.3
	2349	18.6	2350	21.2	2351	22.3
5-13-59	0743	18.6	0737	21.2	0738	22.2
	1210	18.7	1205	21.3	1206	22.3
	1521	18.7	1522	21.3	1523	22.2
	2054	19.0	2055	21.3	2056	22.2
	2323	19.0	2325	21.3	2326	22.2
5-14-59	0750	19.1	0752	21.3	0753	22.2
	1207	19.0	1208	21.3	1209	22.2
	1639	19.0	1640	21.3	1641	22.2
	2005	19.1	2006	21.3	2007	22.2
	2257	19.0	2259	21.3	2313	22.2
5-15-59	0926	19.1	0927	21.3	0928	22.2
	1252	19.1	1253	21.3	1254	22.2
	1726	19.3	1727	21.3	1728	22.2
	2321	19.1	2322	21.3	2323	22.2
5-16-59	0851	19.2	0852	21.3	0853	22.2
	1217	19.0	1218	21.3	1220	22.2
	1236	19.1	1621	21.3	1622	22.2
	2350	19.1	2352	21.3	2353	22.2
5-17-59	0906	19.1	0909	21.4	0910	22.2
	1214	19.1	1215	21.4	1216	22.2
	1741	19.2	1742	21.4	1743	22.2
	2301	19.2	2302	21.4	2303	22.2

Table 32. Continued.

Day	0.5 cm		5.0 cm		16 cm	
	Hour	Temp. (°C)	Hour	Temp. (°C)	Hour	Temp. (°C)
5-18-59	0933	19.1	0935	21.4	0936	22.2
	1124	19.3	1125	21.4	1127	22.2
	1707	19.4	1711	21.4	1712	22.2
	2324	19.2	2325	21.4	2326	22.2
5-19-59	0924	19.3	0925	21.4	0926	22.2
	1330	19.2	1333	21.4	1334	22.2
	1708	19.3	1710	21.4	1711	22.2
	2255	19.3	2256	21.4	2257	22.2
5-20-59	0933	19.3	0934	21.4	0936	22.2
	1239	19.3	1240	21.4	1241	22.2
	1705	19.3	1706	21.5	1707	22.2
5-21-59	0040	21.9	0041	22.3	0042	22.2
	0925	19.2	0926	21.4	0927	22.1
	1251	19.5	1252	21.4	1253	22.2
	1655	19.3	1656	21.4	1657	22.2
	2258	19.3	2303	21.4	2304	22.2
5-22-59	0925	19.3	0926	21.5	0929	22.2
	1256	19.3	1255	21.4		
	1703	19.2	1704	21.4	1705	22.2
	2336	19.3	2337	21.5	2338	22.2
5-23-59	0922	19.3	0923	21.4	0924	22.2
	1309	19.4	1310	21.5	1311	22.2

Table 33. Run 14A. Basic data on the evaporation of water from the soil column and its replenishment from the "water table."

Day	Hour of day	Time since last reading Δt (hrs)	Time since expt. began (hrs)	Water evaporated ΔQ (gms)	Rate of evaporation $\Delta Q / \Delta t$ (gm/hr)	Running total of evap., Q (gms)	H_2O uptake from reservoir (cc)	Rate of H_2O uptake by sample (cc/hr)	Running total of uptake (cc)
5-28-59	1345		.75	3.00	4.00	3.00			
	1430	.75	1.50	2.60	3.47	5.60			
	1536	1.10	2.60	3.40	3.09	9.00			
	1700	1.40	4.00	4.37	3.12	13.37	1.4	0.35	1.4
	2045	3.75	7.75	10.78	2.87	24.15			
	2345	3.00	10.75	8.43	2.81	32.58	3.9	0.58	5.3
5-29-59	0745	8.00	18.75	21.65	2.71	54.23	8.6	1.08	13.9
	1045	3.00	21.75	7.75	2.58	61.98	2.9	0.97	16.8
	1400	3.25	25.00	8.15	2.51	70.13	3.5	1.08	20.3
	1730	3.50	28.50	8.57	2.45	78.70	4.1	1.17	24.4
	2245	5.25	33.75	12.45	2.37	91.15	7.1	1.35	31.5
5-30-59	0830	9.75	43.50	21.16	2.17	112.31	10.5	1.08	42.0
	1930	11.00	54.50	20.68	1.88	132.99	12.0	0.92	54.0
	2348	4.30	58.80	7.54	1.75	140.53	6.9	1.60	60.9
5-31-59	0845	8.95	67.75	14.95	1.67	155.48	8.3	0.93	69.2
	1400	5.25	73.00	8.17	1.56	163.65	5.1	0.97	74.3
	2345	9.75	81.25	12.68	1.30	176.33	9.9	1.02	84.2
6- 1-59	0800	8.25	91.00	10.00	1.21	186.33	9.0	1.09	93.2
	1300	5.00	96.00	5.81	1.16	192.14	4.2	0.84	97.4
	1700	4.00	100.00	4.68	1.17	196.82	5.4	1.35	102.8
	2354	6.90	106.90	7.50	1.09	204.32	6.5	0.94	109.3
6- 2-59	0830	8.60	115.50	9.30	1.08	213.62	8.5	0.99	117.8
	1700	8.50	124.00	9.08	1.07	222.70	7.9	0.93	125.7
6- 3-59	0006	7.10	131.10	7.36	1.04	230.06	6.2	0.87	131.9
	0830	8.40	139.50	8.79	1.05	238.85	8.6	1.02	140.5
	1703	8.55	148.05	8.71	1.02	247.56	7.6	0.89	148.1
	2215	5.20	153.25	5.14	0.99	252.70	5.3	1.02	153.4
6- 4-59	0745	9.50	162.75	9.07	0.95	261.77	6.8	0.72	160.2

Table 34. Run 14A. The distribution of moisture in the soil column as a function of time and distance from the evaporating surface.

Day	Hour of day	Tensiometer Readings[a] (cm Hg at porous cups at given dist. from evaporating surface) 2 cm	4 cm	12 cm	16 cm	24 cm
5-28-59	1256	2.3	2.3	2.3	2.3	2.3
	1345	3.2	2.9	2.7	2.3	2.2
	1430	4.2	3.6	3.4	2.8	2.6
	1536	5.5	4.7	4.4	3.5	3.2
	1700	7.1	5.9	5.4	4.3	3.8
	2045	11.0	8.8	7.7	6.0	4.9
	2345	14.1	11.2	9.1	7.0	5.4
5-29-59	0745	19.8	12.7	12.1	9.0	6.1
	1045	30.2	20.7	12.9	9.5	6.3
	1400	37.0	24.1	13.9	10.0	6.4
	1730	45.5	28.3	14.9	10.9	6.6
	2245	55.9	33.6	16.5	11.7	7.0
5-30-59	0830	58.9	41.9	19.1	13.1	7.1
	1930	59.3	48.0	21.0	15.1	7.9
	2348	59.4	48.9	21.2	14.9	7.3
5-31-59	0845	59.5	50.7	22.2	15.9	7.8
	1400		52.3	22.7	16.3	7.9
	2345		54.4	23.7	16.9	8.0
6- 1-59	0800		55.8	24.1	17.8	8.2
	1300		56.1	24.2	18.0	8.0
	1700		56.2	24.2	18.1	7.9
	2354		56.7	23.3	18.8	7.9
6- 2-59	0830		57.2	23.7	19.0	7.9
	1700		57.2	23.4	19.6	7.8
6- 3-59	0006		57.7	23.4	19.6	7.7
	0830		57.9	22.3	20.2	7.6
	1703			21.7	20.0	7.3
	2215			20.6	19.5	7.2
6- 4-59	0745			20.7	21.3	8.2

[a]Tensiometers at 8 and 30 cm not operating properly.

Table 35. Run 14A. The distribution of temperature in the soil column as a function of time and distance from the evaporating surface.

Day	0.5 cm		5.0 cm		16 cm	
	Hour	Temp. (°C)	Hour	Temp. (°C)	Hour	Temp. (°C)
5-28-59	1251	37.7	1252	37.7	1253	37.7
	1303	35.3				
	1304	34.7				
	1305	34.3	1306	37.7		
	1310	32.7	1312	37.5		
	1315	31.7	1317	37.3		
	1322	30.9	1323	37.1		
	1329	30.4	1330	36.8		
	1333	30.2	1334	36.6	1335	37.7
	1340	30.0	1341	36.4		
	1357	29.6	1358	36.2	1400	37.7
	1402	29.5				
	1429	29.3				
	1437	29.4	1438	35.8	1439	37.7
	1532	29.4	1533	35.8	1534	37.6
	1708	29.5	1709	35.6	1710	37.5
	2041	29.7	2042	35.5	2043	37.4
	2340	29.9	2341	35.4	2342	37.3
5-29-59	0737	30.3	0738	35.6	0739	37.4
	1041	30.4	1042	35.6	1043	37.4
	1729	31.0	1732	36.0	1733	37.6
	2241	31.0	2242	35.8	2243	37.5
5-30-59	0822	31.2	0823	35.5	0824	37.1
	1928	32.5	1929	36.4		
	2343	32.5	2344	36.2	2345	37.4
5-31-59	0842	33.0	0843	36.4	0844	37.5
	1359	33.8	1400	36.7	1401	37.6
	2337	34.2	2338	36.5	2338	37.5
6- 1-59	0759	34.5	0802	36.8	0803	37.5
	1253	34.5	1254	36.7	1255	37.5
	1655	34.5	1656	36.5	1657	37.4
	2345	34.8	2346	36.9	2347	37.6
6- 2-59	0827	34.9	0826	36.9	0828	37.5
	1655	35.1	1656	37.2	1657	37.8
	0002	35.2	0003	37.3	0004	37.6
	0826	35.3	0827	37.5	0828	37.9
	1658	35.2	1659	37.2	1659	37.7
	2205	35.3	2206	37.2	2207	37.5
6- 3-59	0734	35.6	0735	37.5	0736	37.7

Table 36. Run 16A. Basic data on the evaporation of water from the soil column and its replenishment from the "water table."

Day	Hour of day	Time since last reading Δt (hrs)	Time since expt. began (hrs)	Water evaporated ΔQ (gms)	Rate of evaporation $\Delta Q/\Delta T$ (gm/hr)	Running total of evap., Q (gms)	H_2O uptake from reservoir (cc)	Rate of H_2O uptake by sample (cc/hr)	Running total of uptake (cc)
6- 9-59	0945		.75	1.60	2.13	1.60			
	1030	.75	1.50	1.16	1.55	2.76			
	1200	1.50	3.00	2.13	1.42	4.89			
	1400	2.00	5.00	2.78	1.39	7.67			
	1700	3.00	8.00	4.24	1.41	11.91			
	2000	3.00	11.00	3.93	1.31	15.84			
6-10-59	0000	4.00	15.00	5.20	1.30	21.04			
	0830	8.50	23.50	10.77	1.27	31.81	7.5	.30	7.5
	1500	6.50	30.00	8.00	1.23	39.81	3.8	.58	11.3
6-11-59	0000	9.00	39.00	10.56	1.17	50.37			
	0930	9.50	48.50	10.71	1.13	61.08	15.4	.84	26.7
	2100	11.50	60.00	12.24	1.06	73.32			
6-12-59	0930	12.50	72.50	12.67	1.01	85.99	13.9	1.11	40.6
	2115	11.75	84.25	11.35	0.97	97.34			
6-13-59	0900	11.75	96.00	10.77	0.92	108.11			
	2200	13.00	109.00	11.32	0.87	119.43	22.8	.97	63.4

Table 37. Run 16A. The distribution of moisture in the soil column as a function of time and distance from the evaporating surface.

Tensiometer Readings

Day	Hour of day	(cm Hg at porous cups at given dist. from evaporating surface) 4 cm	8 cm	12 cm	24 cm	30 cm
6- 9-59	0854	.8	.8	.9	1.3	1.8
	0945	.6	.6	.7	1.1	1.8
	1030	.8	.9	1.0	1.2	1.8
	1200	1.4	1.5	1.6	1.8	2.1
	1400	2.2	2.4	2.3	2.5	2.5
	1700	3.6	3.6	3.6	3.4	3.4
	2000	4.8	4.9	4.7	4.3	4.1
6-10-59	0000	6.5	6.3	6.1	5.3	5.0
	0830	14.9	14.0	13.6	6.7	6.4
	1500	12.6	10.8	10.1	7.3	7.0
6-11-59	0000	16.4	13.0	12.1	7.7	7.6
	0930	20.7	15.0	13.7	8.1	8.0
	2100	26.2	17.1	15.5	8.1	8.0
6-12-59	0930	32.5	19.3	17.3	8.4	8.3
	2115	38.3	21.2	18.9	8.5	8.4
6-13-59	0900	43.6	23.0	20.3	8.6	8.5
	2200	48.1	24.5	21.6	8.4	8.4
6-14-59	0900	50.8	25.7	22.6	9.0	8.8

Table 38. Run 16A. The distribution of temperature in the soil column as a function of time and distance from the evaporating surface.

Day	0.5 cm		5.0 cm		16 cm	
	Hour	Temp. (°C)	Hour	Temp. (°C)	Hour	Temp. (°C)
6- 9-59	0858	12.7	0859	12.7	0902	12.7
	0913	10.9	0915	12.5	0917	12.7
	0928	10.1	0929	12.2	0931	12.7
	1004	9.5	1005	11.8	1007	12.7
	1028	9.3	1029	11.7	1030	12.7
	1048	9.3	1049	11.6	1050	12.7
	1156	9.2	1157	11.6	1158	12.7
	1356	9.1	1357	11.6	1359	12.7
	1657	8.6	1658	11.5	1659	12.7
	1955	9.1	1956	11.5	1958	12.6
	2351	9.0	2352	11.5	2353	12.6
6-10-59	0827	8.8	0828	11.5	0829	12.7
	1500	8.9	1506	11.5	1507	12.7
6-11-59	0004	9.2	0005	11.6	0006	12.6
	0927	9.2	0928	11.6	0929	12.6
	2056	9.2	2058	11.6	2059	12.7
6-12-59	0923	9.2	0924	11.6	0925	12.6
	2111	9.3	2112	11.6	2113	12.7
6-13-59	0852	9.5	0853	11.7	0854	12.7
	2159	9.6	2200	11.7	2206	12.7
6-14-59	0859	9.8	0907	11.7	0906	12.6
	0009	9.9	0010	11.8	0011	12.8

Table 39. Run 3B. Basic data on the evaporation of water from the soil column.

Day	Hour of day	Time since last reading Δt (hrs)	Time since expt. began (hrs)	Water evaporated ΔQ (gms)	Rate of evaporation $\Delta Q/\Delta t$ (gm/hr)	Running total of evap., Q (gms)
9-30-58	1304		1.07	3.24	3.03	3.24
	1530	2.43	3.50	6.58	2.71	9.82
	2000	4.50	8.00	11.08	2.46	20.90
	2300	3.00	11.00	7.35	2.45	28.25
	0030	1.50	12.50	3.65	2.43	31.90
10-1-58	0833	8.05	20.55	17.20	2.14	49.10
	1300	4.45	25.50	10.50	2.36	59.60
	1700	4.00	29.00	9.55	2.39	69.15
	2325	6.42	35.42	14.07	2.19	83.22
10-2-58	0845	9.33	44.75	20.60	2.21	103.82
	1303	4.30	49.05	8.19	1.90	112.01
	1708	4.09	53.14	8.70	2.13	120.71
	2300	5.86	59.00	9.90	1.69	130.61
10-3-58	0830	9.50	68.50	13.60	1.43	144.21
	1436	6.10	74.60	6.70	1.10	150.91
	2030	5.90	80.50	6.80	1.15	157.71
10-4-58	0000	3.50	84.00	3.33	.95	161.04
	0951	9.85	93.85	8.44	.86	169.48
	1800	8.15	102.00	5.72	.70	175.20
	2300	5.00	107.00	5.08	1.02	180.28
10-5-58	1530	16.50	123.50	11.85	.72	192.13
	2206	6.60	130.10	4.05	.61	196.18
10-6-58	0841	10.57	140.67	5.66	.54	201.84
	1415	5.58	146.25	2.72	.49	204.56
	2230	8.25	154.50	4.55	.55	209.11
10-7-58	1021	11.85	166.35	5.80	.49	214.91
	1705	6.73	173.08	3.19	.47	218.10
	2300	5.92	179.00	2.46	.42	220.56
10-8-58	1700	18.00	197.00	8.00	.44	228.56
	2000	3.00	200.00	1.48	.49	230.04

Table 40. Run 3B. The distribution of moisture in the soil column as a function of time and distance from the evaporating surface.

Tensiometer Readings[a]

Day	Hour of day	(cm Hg at porous cups at given dist. from evaporating surface) 4 cm	8 cm	12 cm	16 cm
9-30-58	1200	0.6	0.6	0.6	0.6
	1304	0.8	0.9	0.7	0.7
	1530	4.1	4.0	4.0	4.0
	2000	10.6	10.5	10.6	10.9
	2300	14.1	13.7	13.8	14.0
10- 1-58	0030	15.5	15.0	15.0	15.2
	0833	20.8	20.0	19.5	19.5
	1300	23.1	22.1	21.2	20.8
	1700	25.2	23.9	22.9	22.3
	2325	29.3	27.3	26.3	25.6
10- 2-58	0845	37.3	33.3	31.7	31.0
	1303	41.5	36.4	34.3	33.5
	1708	45.3	39.4	36.9	36.1
	2300	49.8	43.6	40.7	39.9
10- 3-58	0830	53.3	48.8	45.9	45.5
	1436	54.2	50.3	48.6	48.3
	2030	54.8	52.3	50.5	50.5
10- 4-58	0000	55.1	53.0	51.4	51.6
	0951	55.6	54.4	53.3	53.7
	1800		54.7	54.0	54.4
	2300		54.9	54.3	54.8
10- 5-58	1530		55.4	55.1	55.6
	2206			55.3	55.8
10- 6-58	0841			55.9	56.2

[a]Tensiometer at 2 cm was not functioning.

Table 41. Run 5B. Basic data on the evaporation of water from the soil column.

Day	Hour of day	Time since last reading Δt (hrs)	Time since expt. began (hrs)	Water evaporated ΔQ (gms)	Rate of evaporation $\Delta Q/\Delta t$ (gm/hr)	Running total of evap., Q (gms)
11-29-58	0954		.90	4.25	4.72	4.25
	1324	3.50	4.40	13.24	3.01	17.29
	1642	3.30	7.70	12.08	3.66	29.57
11-30-58	0000	7.30	15.00	27.06	3.71	56.63
	0848	8.80	23.80	24.47	2.78	81.10
	1854	10.10	33.90	30.23	2.99	111.33
12- 1-58	0000	5.10	39.00	15.48	3.04	126.81
	0800	8.00	47.00	20.61	2.58	147.42
	1921	11.35	58.35	21.69	1.91	169.11
12- 2-58	0040	5.32	63.67	7.08	1.33	176.19
	1300	12.33	76.00	13.60	1.10	189.79
12- 3-58	0240	13.67	89.67	10.00	0.73	199.79
	2124	18.73	108.40	12.06	0.64	211.85
12- 4-58	0900	11.60	120.00	5.65	0.49	217.50
12- 5-58	1051	25.85	145.85	6.81	0.26	224.31
12- 6-58	0039	13.80	159.65	2.88	0.21	227.19
	1930	18.85	178.50	3.48	0.18	230.67

Table 42. Run 5B. The distribution of moisture in the soil column as a function of time and distance from the evaporating surface.

Tensiometer Readings

Day	Hour of day	(cm Hg at porous cups at given dist. from evaporating surface) 2 cm	4 cm	8 cm	12 cm	16 cm
11-29-58	0900	0.4	0.4	0.4	0.4	0.4
	0954	1.3	1.3	1.2	1.2	1.0
	1324	6.1	5.9	5.5	5.3	5.1
	1642	11.3	11.0	10.4	10.1	9.8
11-30-58	0000	22.2	20.8	19.0	18.4	17.9
	0848	35.8	31.8	27.0	20.0	19.1
	1854	54.2	49.3	40.3	36.3	34.2
12- 1-58	0000		54.7	47.1	42.8	40.5
	0800		56.2	53.0	49.6	47.5
	1921			56.2	54.5	53.1
12- 2-58	0040					54.5

Table 43. Run 6B. Basic data on the evaporation of water from the soil column.

Day	Hour of day	Time since last reading Δt (hrs)	Time since expt. began (hrs)	Water evaporated ΔQ (gms)	Rate of evaporation $\Delta Q / \Delta t$ (gm/hr)	Running total of evap., Q (gms)
1-6-59	1030		1.50	6.87	4.58	6.87
	1236	2.10	3.60	8.11	3.86	14.98
	1715	4.65	8.25	16.25	3.49	31.23
	2145	4.50	12.75	14.44	3.21	45.67
1-7-59	0000	2.25	15.00	7.96	3.54	53.63
	0830	8.50	23.50	27.96	3.29	81.59
	1048	2.30	25.80	6.93	3.00	88.52
	1230	1.70	27.50	5.70	3.35	94.22
	1530	3.00	30.50	9.20	3.07	103.42
	2100	5.50	36.00	15.05	2.74	118.47
1-8-59	0000	3.00	39.00	7.09	2.36	125.56
	0836	8.60	47.60	18.65	2.17	144.21

Table 44. Run 6B. The distribution of moisture in the soil column as a function of time and distance from the evaporating surface.

Tensiometer Readings

Day	Hour of day	(cm Hg at porous cups at given dist. from evaporating surface) 2 cm	4 cm	8 cm	12 cm	16 cm
1-6-59	0850	3.8	3.8	3.8	3.8	3.8
	1030	6.7	6.4	6.0	5.8	5.6
	1236	10.3	9.8	9.2	8.9	8.5
	1715	17.6	16.4	15.2	14.7	14.1
	2145	23.7	21.1	18.9	18.1	17.3
1-7-59	0000	27.2	23.4	20.5	19.4	18.6
	0830	43.6	34.1	26.3	23.2	
	1048	47.8	37.0	27.2	23.5	21.9
	1230	50.1	39.3	28.7	24.8	23.3
	1530	53.3	43.5	31.8	27.2	25.2
	2100	54.6	48.5	36.8	31.3	28.7
1-8-59	0000	55.0	50.6	39.0	33.8	31.0
	0836		53.5	45.3	39.8	37.1

Table 45. Run 7B. Basic data on the evaporation of water from the soil column.

Day	Hour of day	Time since last reading Δt (hrs)	Time since expt. began (hrs)	Water evaporated ΔQ (gms)	Rate of evaporation $\Delta Q / \Delta t$ (gm/hr)	Running total of evap., Q (gms)
6-10-59	1045		.75	4.00	5.33	4.00
	1200	1.25	2.00	5.90	4.72	9.90
	1400	2.00	4.00	9.00	4.50	18.90
	1530	1.50	5.50	6.37	4.25	25.27
	1700	1.50	7.00	6.26	4.17	31.53
	2030	3.50	10.50	14.15	4.04	45.68
	2315	2.75	13.25	11.35	4.13	57.03
6-11-59	0815	9.00	22.25	36.78	4.09	93.81
	1142	3.45	25.70	13.86	4.02	107.67
	1354	2.20	27.90	8.90	4.50	116.57
	1700	3.10	31.00	12.14	3.92	128.71
6-12-59	0000	7.00	38.00	26.20	3.74	154.91
	0830	8.50	46.50	28.90	3.40	183.81
	1300	4.50	51.00	12.61	2.80	196.42
	1700	4.00	55.00	8.32	2.08	204.74
	2300	6.00	61.00	10.35	1.72	215.09
6-13-59	0815	9.25	70.25	12.80	1.38	227.87
	1745	9.50	79.75	10.60	1.12	238.49
6-14-59	0030	6.75	86.50	6.70	0.99	245.19
	0930	9.00	95.50	8.43	0.94	253.62
	1900	9.50	105.00	7.35	0.77	260.97
6-15-59	0700	12.00	117.00	8.05	0.67	269.02

Table 46. Run 7B. The distribution of moisture in the soil column as a function of time and distance from the evaporating surface.

Tensiometer Readings

Day	Hour of day	(cm Hg at porous cups at given dist. from evaporating surface) 2 cm	4 cm	8 cm	12 cm	16 cm
6-10-59	1000	.5	.5	.6	.4	.3
	1045	1.8	1.4	1.5	1.2	1.2
	1200	3.9	3.6	3.6	3.2	3.1
	1400	7.5	7.2	7.2	6.6	6.6
	1530	9.9	9.5	9.5	9.0	8.8
	1700	12.7	12.4	12.2	11.6	11.4
	2030	18.9	18.5	18.1	17.2	16.9
	2315	23.0	22.3	21.6	20.6	20.1
6-11-59	0815	34.6	32.4	29.7	27.5	26.6
	1142	41.9	38.1	33.8	30.9	29.5
	1354	48.1	42.7	36.9	33.2	31.6
	1700	55.9	49.8	42.0	37.1	34.9
6-12-59	0000	58.9	57.4	51.9	45.5	42.9
	0830		58.4	57.8	52.5	50.8
	1300			58.3	54.7	53.5
	1700				56.1	55.0
	2300				57.4	56.6
6-13-59	0815				58.2	57.7

Table 47. Run 7B. The distribution of temperature in the soil column as a function of time and distance from the evaporating surface.

Day	-0.5 cm		1 cm		2 cm		4 cm		6 cm		9 cm		13 cm		16 cm	
	Hour	Temp. (°C)	Hour	Temp. (°C)	Hour	Temp. (°C)	Hour	Temp. (°C)	Hour	Temp. (°C)	Hour	Temp. (°C)	Hour	Temp. (°C)	Hour	Temp. (°C)
6-10-59	0841	37.7	0842	37.7	0845	37.7	0846	37.7	0847	37.7	0848	37.7	0850	37.7		37.7
	1008	33.0	1009	33.6	1010	35.4	1011	37.5	1011	37.7	1012	37.7	1013	37.7		37.7
	1014	32.3	1015	32.1	1016	34.3	1017	36.8	1018	37.6	1019	37.7	1020	37.7		37.7
	1022	32.1	1022	31.2	1023	33.3	1024	36.2	1025	37.3	1026	37.7	1027	37.8		37.7
	1029	32.1	1029	30.9	1030	33.0	1031	35.9	1032	37.8	1033	37.7	1034	37.8		37.7
	1036	31.8	1037	30.5	1037	32.4	1038	35.5	1039	37.6	1040	37.7	1041	37.8		37.7
	1052	31.6	1053	30.1	1053	32.0	1054	35.0	1055	36.6	1056	37.3	1057	37.8		37.7
	1110	31.6	1110	30.0	1111	31.9	1111	34.7	1112	36.4	1113	37.2	1114	37.9		37.7
	1143	32.0	1144	30.0	1144	31.7	1145	34.6	1146	36.2	1147	37.3	1148	37.7		37.6
	1203	32.0	1204	30.0	1205	31.9	1205	34.6	1206	36.2	1207	37.0	1208	37.7		37.6
	1405	32.0	1406	29.9	1407	31.7	1407	34.5	1408	36.1	1409	36.9	1410	37.6		37.6
	1533	31.9	1534	29.7	1536	31.5	1536	34.3	1537	35.9	1538	36.8	1539	37.6		37.4
	2027	32.0	2028	29.4	2029	31.1	2030	33.9	2032	35.3	2033	36.4	2035	37.3		37.2
	2307	32.3	2308	29.6	2310	31.3	2311	34.0	2312	35.7	2313	36.9	2314	37.6		37.3
6-11-59	0805	32.3	0806	29.5	0807	31.1	0808	33.9	0809	35.7	0810	36.8	0811	37.5		37.2
	1134	32.3	1134	29.6	1135	31.3	1136	34.0	1136	35.8	1137	37.0	1138	37.6		37.3
	1348	32.3	1349	29.4	1350	31.2	1350	33.9	1351	35.7	1352	37.0	1353	37.6		37.2
	1702	32.3	1703	29.6	1704	31.2	1705	34.0	1705	35.7	1706	36.7	1707	37.5		37.2
	2349	32.6	2350	29.6	2350	31.3	2351	34.0	2351	35.7	2352	36.9	2353	37.5		37.4
6-12-59	0822	33.3	0823	30.4	0823	32.1	0824	34.6	0825	36.1	0826	37.1	0827	37.6		37.3
	1259	34.4	1259	31.9	1300	33.3	1305	35.3	1306	36.4	1306	37.2	1307	37.5		37.5
	1703	35.5	1704	33.4	1705	34.6	1706	36.0	1707	37.0	1708	37.6	1708	37.6		37.6
	2253	36.0	2252	34.1	2251	35.1	2254	36.2	2254	37.0	2255	37.5	2255	37.7		37.4
6-13-59	0819	36.6	0820	35.0	0820	35.8	0821	36.5	0822	37.3	0823	37.8	0824	38.0		37.6
	1740	36.9	1741	35.8	1742	36.4	1742	36.8	1743	37.4	1744	37.8	1744	38.1		37.0
6-14-59	0022	37.0	0023	35.9	0023	37.3			0025	37.4	0026	37.8	0027	38.1		37.7
	0922	37.3	0923	36.5	0924	36.7	0925	36.9	0926	37.4	0927	37.9	0927	38.1		37.7
	1859	37.4	1900	36.8	1901	37.0	1902	37.0	1903	37.5	1904	37.9	1904	38.1	1905	37.7

6-15-59	0656 37.7	0658 37.2	0659 37.1	0700 37.0	0714 37.5	0717 37.8	0721 38.1	0723 37.7
	1650 37.7	1652 37.7	1654 37.5	1655 37.3	1656 37.6	1658 37.9		1703 37.7
6-16-59	0827 37.8	0828 38.0	0830 37.6	0831 37.1	0832 37.2	0833 37.7	0838 38.0	0839 37.4
	1642 38.0	1644 38.5	1645 38.0	1646 37.5	1647 37.7	1648 38.0	1650 38.1	1651 37.8
6-17-59	0823 37.8	0825 38.5	0826 38.0	0827 37.2	0828 37.4	0829 37.6	0830 37.7	0831 37.2
	1659 37.9	1702 38.2	1704 37.6	1708 37.1	1709 37.5	1711 37.7	1712 37.9	1713 37.6
6-18-59	0850 37.7	0852 37.0	0853 37.0	0854 36.8	0855 37.2	0856 37.5	0857 37.6	0857 37.2
6-19-59	0853 37.5	0854 36.7	0855 36.7	0856 36.6	0857 36.9	0858 37.2	0859 37.5	0900 37.0
	1654 37.4	1655 37.2	1656 37.2	1657 37.0	1658 37.4	1659 37.8	1700 37.9	1701 37.6
6-20-59	0827 37.6	0828 37.2	0828 37.0	0829 36.8	0829 37.1	0830 37.6	0831 37.6	0832 37.2
	1622 37.5	1623 37.6	1624 37.3	1624 37.0	1625 37.4	1626 37.9	1627 38.0	1628 37.6
6-21-59	0949 37.5	0950 37.7	0951 37.4	0952 37.0	0953 37.3	0953 37.6	0954 38.0	0955 37.4
	2125 37.5	2125 37.8	2126 37.6	2126 37.2	2127 37.4	2128 37.9	2128 38.0	2129 37.7
6-22-59	0810 37.7	0811 38.0	0812 37.7	0813 37.2	0814 37.4	0814 37.9	0814 38.1	0815 37.7
	1657 37.7	1658 38.0	1658 38.0	1659 37.4	1700 37.6	1702 37.9	1703 38.1	1703 37.7
	2305 37.5	2306 38.0	2307 37.8	2307 37.2	2308 37.4	2308 37.8	2309 38.1	2310 37.6

Table 48. Run 8B. Basic data on the evaporation of water from the soil column.

Day	Hour of day	Time since last reading Δt (hrs)	Time since expt. began (hrs)	Water evaporated ΔQ (gms)	Rate of evaporation $\Delta Q/\Delta t$ (gm/hr)	Running total of evap., Q (gms)
7-20-59	1345		.75	1.30	1.73	1.30
	1430	.75	1.50	1.20	1.60	2.50
	1630	2.00	3.50	3.10	1.55	5.60
	2000	3.50	7.00	5.14	1.47	10.74
7-21-59	0015	4.25	11.25	6.04	1.42	16.78
	0830	8.25	19.50	11.34	1.37	28.12
	1300	4.50	24.00	6.00	1.33	34.12
	1700	4.00	28.00	5.30	1.32	39.42
7-22-59	0000	7.00	35.00	9.05	1.29	48.47
	1000	10.00	45.00	13.00	1.30	61.47
	1621	6.35	51.35	7.91	1.25	69.38
7-23-59	0030	8.15	59.50	10.22	1.25	79.60
	0900	8.50	68.00	10.50	1.24	90.10
	1700	8.00	76.00	9.70	1.21	99.80
7-24-59	0000	7.00	83.00	8.44	1.21	108.24
	0900	9.00	92.00	10.76	1.20	119.00
	2300	14.00	106.00	16.30	1.16	135.30
7-25-59	1000	11.00	117.00	12.78	1.16	148.08
	2200	12.00	129.00	13.46	1.12	161.54
7-26-59	0900	11.00	140.00	11.90	1.08	173.44
	2200	13.00	153.00	13.85	1.07	187.29
7-27-59	1000	12.00	165.00	12.13	1.01	199.42
	2200	12.00	177.00	10.46	0.87	209.88
7-28-59	0900	11.00	188.00	6.75	0.61	216.63
	2200	13.00	201.00	6.25	0.48	222.88
7-29-59	1000	12.00	213.00	4.90	0.41	227.78
	2300	11.00	224.00	4.34	0.39	232.12
7-30-59	0900	10.00	234.00	3.07	0.31	235.19
	2100	12.00	246.00	3.30	0.28	238.49
7-31-59	0900	12.00	258.00	2.91	0.24	241.40
8- 1-59	0006	15.10	273.10	3.30	0.22	244.70
	1600	15.90	289.00	2.78	0.17	247.48
8- 2-59	1018	18.30	307.30	4.20	0.23	251.68
	2200	11.70	319.00	2.90	0.25	254.58

Table 49. Run 8B. The distribution of moisture in the soil column as a function of time and distance from the evaporating surface.

Tensiometer Readings

Day	Hour of day	(cm Hg at porous cups at given dist. from evaporating surface) 2 cm	4 cm	8 cm	12 cm	16 cm
7-20-59	1250	.4	.4	.4	.4	.4
	1345	.3	.4	.3	.3	.2
	1430	.3	.4	.3	.2	.2
	1630	.6	.6	.5	.5	.5
	2000	1.9	1.9	1.7	1.8	1.7
7-21-59	0015	4.2	4.2	4.0	4.0	3.9
	0830	9.7	9.7	9.3	9.4	9.1
	1300	12.5	12.5	11.9	12.0	11.8
	1700	14.8	14.8	14.5	14.1	13.9
7-22-59	0000	17.7	17.7	16.8	17.0	16.7
	1000	21.9	21.8	20.4	20.5	20.0
	1621	23.7	23.6	22.1	22.0	21.5
7-23-59	0030	26.7	26.3	24.2	24.0	23.4
	0900	30.8	30.0	26.8	26.3	25.4
	1700	33.0	32.3	28.7	28.3	27.3
7-24-59	0000	33.8	32.8	29.5	29.2	28.4
	0900	37.4	36.0	31.6	31.0	30.0
	2300	48.5	44.6	36.5	35.0	33.1
7-25-59	1000	57.1	52.4	41.3	39.0	36.3
	2200	58.5	57.1	46.8	43.6	40.4
7-26-59	0900		58.3	50.9	47.8	44.1
	2200		58.7	55.2	52.0	47.8
7-27-59	1000			57.3	55.0	51.1
	2200			57.8	56.4	53.5
7-28-59	0900			58.4	57.6	55.2
	2200			58.7	58.0	56.3
7-29-59	1000			58.7	57.8	57.1
	2300				58.4	57.4
7-30-59	0900				58.6	57.9
	2100				58.8	58.2
7-31-59						58.5

Table 50. Run 8B. The distribution of temperature in the soil column as a function of time and distance from the evaporating surface.

Day	-0.5 cm		1 cm		2 cm		4 cm		6 cm		9 cm		13 cm		16 cm	
	Hour	Temp. (°C)	Hour	Temp. (°C)	Hour	Temp. (°C)	Hour	Temp. (°C)	Hour	Temp. (°C)	Hour	Temp. (°C)	Hour	Temp. (°C)	Hour	Temp. (°C)
7-20-59	1252	12.7	1254	12.7	1256	12.7	1257	12.7	1259	12.7	1303	12.7	1305	12.7		12.7
	1310	10.2	1312	11.5	1313	11.9	1315	12.4	1316	12.6	1317	12.7	1318	12.7		12.7
	1320	9.8	1321	10.9	1322	11.4	1324	12.1	1325	12.5	1326	12.7	1328	12.7		12.7
	1330	9.5	1331	10.5	1333	11.2	1334	11.8	1336	12.3	1337	12.6	1338	12.7		12.7
	1341	9.5														
	1421	10.0	1423	10.4	1424	11.0	1425	11.7	1428	12.3	1429	12.4	1430	12.9		
	1626	10.2	1628	9.9	1629	10.6	1630	11.3	1634	11.9	1635	12.3	1636	12.7		13.0
	1955	10.4	1957	9.8	1958	10.4	1959	11.2	2003	11.9	2004	12.3	2005	12.7		12.9
7-21-59	0006	10.5	0007	9.8	0008	10.2	0009	11.0	0010	11.9	0012	12.4	0013	12.6		12.7
	0821	10.4	0822	9.7	0824	10.3	0825	10.9	0827	11.8	0828	12.2	0828	12.6		12.7
	1255	10.4	1256	9.6	1257	10.2	1258	10.8	1259	11.6	1300	12.2	1303	12.5		12.5
	1654	10.4	1655	9.7	1655	10.2	1656	10.8	1657	11.7	1658	12.2	1659	12.5		12.5
	2350	10.4	2351	9.7	2353	10.2	2354	10.8	2355	11.7	2356	12.2	2357	12.5		12.5
7-22-59	0955	10.4	0956	9.7	0956	10.1	0957	10.8	0958	11.6	0959	12.2	1000	12.4		12.4
	1612	10.3	1613	9.6	1614	10.1	1615	10.7	1616	11.6	1617	12.1	1618	12.5		12.6
7-23-59	0028	10.3	0029	9.6	0029	10.1	0030	10.8	0031	11.6	0032	12.2	0033	12.5		12.5
	0852	10.3	0853	9.6	0854	10.0	0855	10.8	0856	11.6	0857	12.2	0858	12.4		12.5
	1656	10.4	1657	9.7	1658	10.2	1658	10.8	1659	11.6	1700	12.2	1706	12.4		12.4
	2355	10.4	2356	9.6	2357	10.1	2358	10.8	2359	11.6	2359	12.2	0000	12.5		12.5
7-24-59	0855	10.4	0856	9.7	0857	10.1	0858	10.8	0858	11.6	0859	12.2	0900	12.5		12.5
	2257	10.4	2258	9.7	2258	10.1	2259	10.8	2305	11.6	2306	12.2	2307	12.4		12.4
7-25-59	0956	10.4	0957	9.8	0958	10.2	0959	10.9	1000	11.7	1005	12.3	1006	12.4	1007	12.4
	2202	10.4	2203	9.8	2204	10.2	2205	10.9	2205	11.6	2206	12.2	2207	12.5	2208	12.5
7-26-59	0855	10.4	0856	9.7	0857	10.1	0858	10.9	0859	11.6	0900	12.2	0902	12.2	0903	12.4
	2206	10.3	2207	9.7	2208	10.1	2209	10.8	2210	11.5	2211	12.1	2212	12.4	2213	12.4
7-27-59	0957	10.4	0958	9.9	0959	10.3	1000	10.9	1003	11.6	1004	12.2	1005	12.4		
	2204	10.8	2205	10.3	2206	10.6	2207	11.0	2208	11.7	2208	12.2	2209	12.5	2210	12.5

7-28-59	0856 11.2	0857 10.8	0858 10.9	0859 11.2	0900 11.8	0902 12.3	0903 12.4	0904 12.4
	2159 11.4	2149 10.9	2152 11.1	2152 11.3	2153 11.9	2154 12.3	2154 12.4	2155 12.4
7-29-59	0953 11.5	0954 11.0	0955 11.1	0956 11.3	0958 11.9	0958 12.3	0959 12.4	1000 12.4
	2258 11.6	2259 11.1	2300 11.1	2302 11.3	2303 11.9	2304 12.3	2304 12.4	2305 12.4
7-30-59	0854 11.6	0854 11.2	0855 11.2	0856 11.4	0857 11.9	0857 12.3	0858 12.4	0859 12.4
	2100 11.7	2101 11.2	2103 11.2	2104 11.3	2105 11.9	2105 12.3	2106 12.4	2107 12.4
7-31-59	0859 11.8	0900 11.3	0905 11.2	0906 11.3	0907 11.8	0910 12.3	0911 12.4	0912 12.4
	2322 11.8	2323 11.4	2325 11.3	2326 11.3	2327 11.8	2328 12.3	2329 12.4	2330 12.3
8- 1-59	1548 12.0	1549 11.5	1550 11.4	1551 11.4	1551 11.8	1552 12.2	1552 12.4	1553 12.4
8- 2-59	1010 12.1	1011 12.0	1012 12.0	1213 11.9	1014 12.2	1014 12.4	1014 12.4	1015 12.4
	2203 12.1	2204 11.9	2205 11.9	2206 11.9	2206 12.2	2207 12.4	2207 12.4	2208 12.3
8- 3-59	0954 12.1	0955 11.9	0956 11.9	0957 11.9	0957 12.2	0958 12.4	0959 12.4	0959 12.3

Table 51. Series B. Distribution of moisture in the column as determined by gravimetric sampling at the end of the run.

Distance from evap. surface at midpoint of the sampling interval (cm)	% Moisture by wt. (oven-dry basis) Run 3B (gm/gm)	Run 6B (gm/gm)	Run 8B (gm/gm)
.5	2.37	10.32	5.19
1.5	5.21	14.02	8.51
2.5	8.67	15.01	10.50
3.5	9.86	15.95	11.11
4.5	10.76	16.52	11.90
5.5	10.88	16.78	12.63
6.5	11.47	17.22	13.04
7.5	11.54	17.39	13.94
8.5	11.87	17.47	13.99
9.5	12.00	17.76	14.12
10.5	12.04	17.96	14.28
11.5	12.10	18.06	14.46
12.5	12.13	18.23	14.57
13.5	11.98	18.19	14.54
14.5	12.27	18.20	14.58
15.5	12.41	18.39	14.58
16.5	12.44	18.30	14.62
17.5	12.57	18.49	14.87
Duration of run (hrs)	200.0	47.6	319.0
Temperature of bath (^{o}C)	24.9	34.9	12.7
Bulk density of sample (gm/cm^3)	1.40	1.40	1.40
Initial moisture suction (cm Hg)	0.6	3.8	0.4

APPENDIX II

Propositions

Propositions[a]

1. Many non-reproducible experimental results for heats of wetting, adsorption isotherms, and surface areas can be explained on the basis of slight differences in the initial moisture contents of the samples.

2. The classical work of Brown and Escombe (1900) on diffusion through porous septa is usually misinterpreted.

3a. The rate determining process for the approach to equilibrium in the case of adsorption of water on dry colloidal materials in vacuo is the dissipation of heat rather than the rate of condensation or uptake of water vapor,

b. or, little success can be expected in studying the kinetics of adsorption of moisture by soils using "high vacuum" techniques.

4. The resistance to water flow through the conducting tissue of plants is small in comparison to the resistance that exists in the region between the root hair and the xylem.

5. Researchers have been careless in designating the "driving force" in evaporation of water and, in fact, often mistake it completely.

6. More class time should be spent in doing things other than giving and taking notes. The situation could be largely remedied by carefully prepared lecture outlines available to the students through the college bookstore.

7. Emphasis on operational definitions is warranted even if they do fall short of the theoretical ideal.

8. Air entry into soil during drying merits more attention than it has received to date in analyses of drying; it is a more serious problem in laboratory than in field studies.

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[a]The defense of several propositions is a portion of the final examination of candidates for the Ph. D. degree in Agronomy at Utah State University.

Proposition No. 1

Many non-reproducible experimental results for heats of wetting, adsorption isotherms, and surface areas can be explained on the basis of slight differences in the initial moisture contents of the samples.

Surface Areas and Adsorption Isotherms

Several different groups of workers, none of whom were aware of the dilema of the others, have encountered the problem of the effect of the initial moisture content of the sample on the results of sorption experiments. The riddle is: Why should relatively small variations in initial moisture content have such a tremendous effect on the adsorption process?

Mooney, Keenan, and Wood (1952) found on repeated adsorption-desorption measurements of water vapor on montmorillonite that the desorption isotherms were reproducible whereas the adsorption isotherms depended on the initial water content of the sample. The problem was so serious that it forced these workers to use desorption isotherms exclusively in their analysis. They offered the possible explanation that when the clay is "practically dry", surface inhomogeneities cause the system to be very sensitive to slight variations of residual water present.

Barrer and Mackenzie (1954) demonstrated in their kinetic studies that the sorptive properties of attapulgite toward other species which included N_2, O_2, CO_2, NH_3, CH_3OH, and C_2H_5OH were linked with its water content. Note that this effect, although probably hysteresis-linked, is not the hysteresis main effect; these workers found that hysteresis was "very slight" if the samples had been initially outgassed at temperatures close to those of subsequent sorption. They considered that crystal imperfections result in cations being sparsely distributed along the channels, which together with water molecules provide high energy barriers opposing diffusion, even a few of which could inhibit entry into the intracrystalline channels by reducing the diffusion rate to a negligible value.

Some of the data of Barrer and Mackenzie is presented in Figures 18, 19, and 20. Figure 18 shows the marked difference in water loss as a function of temperature depending upon whether degassing was performed under atmospheric or vacuum pressure conditions. They also found that as the initial outgassing temperature increased the sorption equilibrium in subsequent low temperature isotherms was established with increasing slowness and that lower equilibrium values resulted. The latter effect is shown in Figure 19. A third effect noted by these workers is that, as shown in Figure 20, the equilibrium uptake is very sensitive to the duration of outgassing. All these factors--pressure, duration and temperature of outgassing--affect the moisture content of the sample.

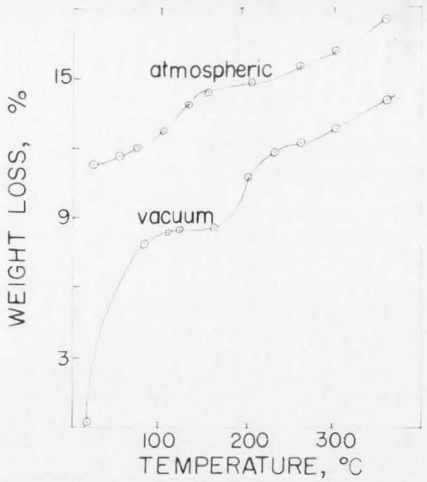

Figure 18. Loss of volatile matter from attapulgite as a function of outgassing temperature for atmospheric and vacuum outgassing. (From Barrer and Mackenzie, 1954, Figure 1a)

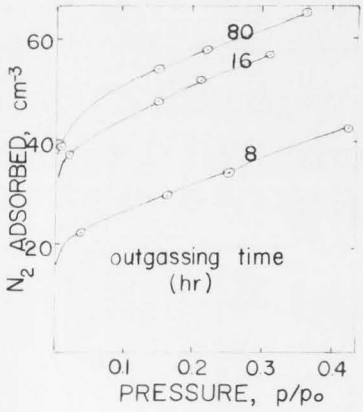

Figure 19. Effect of duration of outgassing at room temperature upon subsequent N_2 sorption by attapulgite at -194° C. (From Barrer and Mackenzie, 1954, Figure 2c)

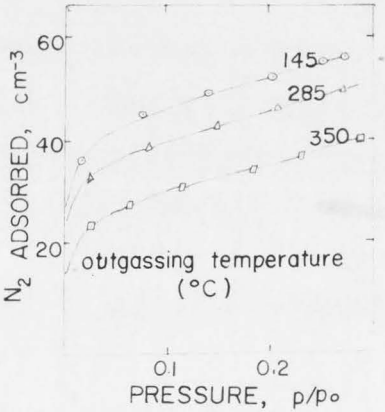

Figure 20. Effect of temperature of outgassing upon subsequent sorption of N_2 by attapulgite at -194° C. (From Barrer and Mackenzie, 1954, Figure 2d)

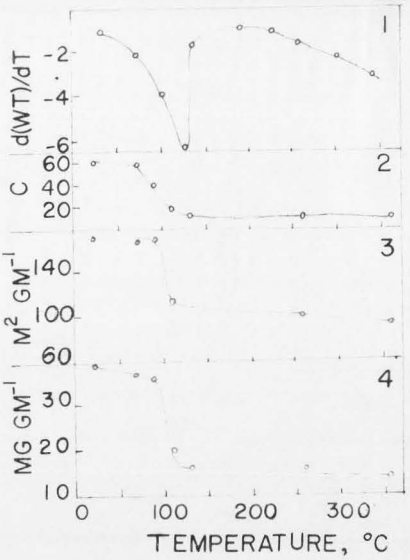

Figure 21. Correlation of various properties of pentane sorption with outgassing temperature: (1) water loss from attapulgite, (2) C value, (3) surface area, (4) amount sorbed at relative pressure 0.1. (From Barrer, Mackenzie, and MacLeod, 1954, Figure 3)

Barrer, Mackenzie, and McLeod (1954) found that a close relationship exists among the temperature coefficient of water loss, the C parameter of the B.E.T. theory equation, surface areas, and the amount of pentane adsorbed at relative pressures of 0.1 at various temperatures of outgassing. The inter-relationships are shown in Figure 21. It may be noted that the rate of water loss is rapid at the standard oven-drying temperature of 105 - 110 °C used by soils workers.

According to Tomes, Hunt, and Blaine (1957), Powers and Brownyard (1946) found that the ratio v_m/w_n, where v_m is the amount of material required to form a monolayer of the sorbate in the B.E.T. equation,

$$\frac{p}{v\,(p_o - p)} = \frac{1}{v_m\,C} + \frac{C - 1}{v_m\,C}\,\frac{p}{p_o}\ ,$$

and w_n is the nonevaporable water content of hydrated cement, was nearly constant. [In the equation, p is the vapor pressure of water in equilibrium with the specimen, p_o is the vapor pressure of pure water at the same temperature, C is a constant related to ΔH adsorption, v is the amount of water adsorbed per gram of speciman, and v_m is the amount of water required to cover the surface completely with a unimolecular layer.]

The constancy of the ratio v_m/w_n suggests that the surface area computed from water-vapor adsorption data is proportional to the amount of hydration products present. Since Powers and Brownyard had also noticed that successive sorption isotherms on hardened portland cement are not reproducible, Tomes and co-workers concluded that the specific surface of portland cement is a function not only of hydration products but also of the history of the speciman after hydration stops.

In response to the above observations Tomes, et al., (1957) conducted extensive experiments to study (a) the nonreversible vapor sorption behavior of hydrated cement, (b) its behavior when wetted with liquid and dried under vacuum and (c) the manner in which v_m and w_n vary when determined on specimens of the same paste that had been dried for different periods of time.

Nonreversible sorption behavior. Portland cement of water:cement ratio 0.5 was poured into 1 x 5 x 5 cm molds where it hardened for 24 hours. It was then cured in closed quart jars in high humidity for some time. The samples were vacuum dried for two days to stop hydration, broken into small pieces and stored for several months in sealed glass tubes. Before making adsorptions the samples were dried for 6 days from the stored state before exposure to water vapor. They were then subjected to successive adsorption and desorption cycles. In cycles 2 - 7 the specimens were redried to their cycle 1 dry weight before exposure to water vapor. Before cycle 8 was begun they were dried for 41 days.

Figure 22 depicts the change in surface areas of hydrated portland cement of two different size fractions which were carefully taken through 8 cycles of drying and adsorption. It can be seen that the surface area of the powder decreased from 90 $m^2\ gm^{-1}$ on the first cycle to about 56 $m^2\ gm^{-1}$ on the seventh and eighth cycles. These workers concluded that the change is, for the most part, independent of the state of subdivision of the cement. They postulated that "the loss in sorption capacity probably involves small changes in the colloidal structure of the paste." Surface areas by N_2 adsorption also showed decreasing surface areas on successive cycles.

Liquid-wetted and dried under vacuum. In order to compare wetting from the liquid phase with vapor-wetting as in the surface area measurements a number of specimens were wetted by covering them with liquid water for one hour at 21 $\pm$ .2° C after which the water was evaporated by vacuum.

Wetting and drying in this manner produced less change in the water sorptive capacity than was produced by adsorption and desorption of

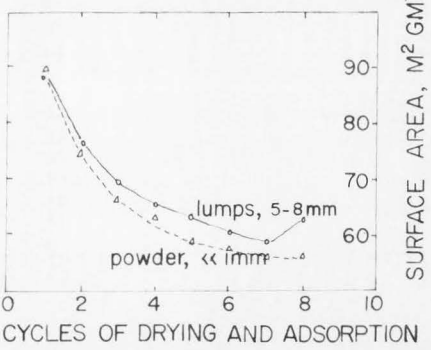

Figure 22. Specific surface by water-vapor adsorption obtained by repeated measurement on specimens of hardened cement paste. (From Tomes, Hunt, and Blaine, 1957, Figure 3)

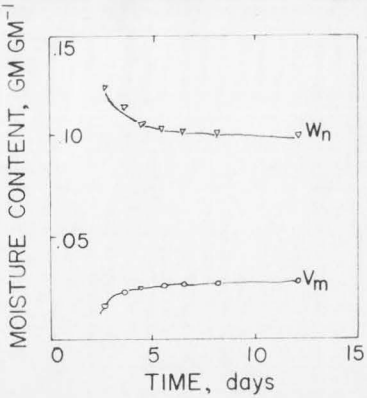

Figure 23. v_m and w_n as functions of drying time. (From Tomes, Hunt, and Blaine, 1957, Figure 4) Note: These data are for the same experiment as the data of Table 52.

Table 52. Dry weights and amounts of water adsorbed by specimens dried for different periods of time.

Specimen[a]	Cumulative drying time[b] (days)	Dry weight (gm water per gm ignited paste)	Grams of water absorbed per gm of ignited paste at relative pressure, p/po 0.0999	0.1478	0.1954	0.2400
7A	2.6	1.1373	0.0147	0.172	0.0192	0.0214
7B	3.5	1.1234	.0233	.0259	.0284	.0305
7C	4.4	1.1186	.0254	.0285	.0304	.0329
7D	5.4	1.1171	.0259	.0289	.0314	.0336
7E	6.4	1.1155	.0264	.0294	.0320	.0341
7F	8.2	1.1145	.0273	.0303	.0329	.0349
7G	12.1	1.1126	.0283	.0312	.0336	.0359

[a]These specimens were obtained from paste that was cured in moist air for 1 week.

[b]Includes two days of vacuum drying of the unground paste to stop hydration.

water vapor. "This difference suggests that the adsorption and desorption process may have occurred in a relative humidity range where shrinkage effects predominated, whereas wetting and drying produced strong swelling and shrinkage during each cycle."

v_m and w_n as functions of drying time. These results are presented in Figure 23 and Table 52. A careful look at Table 52 reveals that the specimens did not resorb all of the water that was removed in the latter stages of drying. Figure 23 indicates that v_m and w_n are reciprocally related. Tomes, Hunt, and Blaine listed several possible reasons for the irreversible sorption behavior of portland cement as:
(a) Coalescense of small particles into larger particles accompanied by a decrease in total capillary volume.
(b) Failure of the lattice to reexpand to its original dimensions if brought back to original temperature and relative humidity conditions.
(c) Polymorphic transformations.
(d) Contamination of the surface.
Their final conclusion was that the changes probably represent shrinkage or other modification of the colloidal structure of the cement paste.

Collis-George found (a) that at any soil moisture suction greater than pF 4, the basal spacings of <1μ Na-montmorillonite samples are larger for drying than they are on wetting (At pF's <4 the basal spacings are 19.2 A whether wetting or drying.), and (b) that even at a total pressure of only 2 cm Hg the H_2SO_4 solution method of humidity control was difficult to use for relative humidities higher than 93%.

Collis-George (1955) summed up the situation of slight differences in initial conditions of samples in stating:

> ... it appears that the discrepancies between the results of various workers using apparently the same, e.g., Na-montmorillonite, can only be accounted for by assuming that either the materials were initially different although superficially similar, or that the method of pre-treatment, however slight, has sufficed to permanently modify their intra-micellar structure. Therefore, until more information is available to explain these differences, it behoves every worker to describe precisely the operations and treatments he carried out.

Heat of Wetting

Among those who have studied the influence of moisture content on heats of wetting are Bouyoucous (1925), Janert (1934), Hoseh (1937), and Puri and Hoon (1939). Some of the data of Hoseh are presented in Figure 24 and Table 53. Figure 24 shows Hoseh's results for heat of wetting of the hydrogen-saturated fine fraction of four California soils as a function of the temperature at which the samples were dried. Data in Table 53 show that the heat of wetting goes through a maximum as the temperature of drying increases. Hoseh concluded that heat of wetting will be evolved as long as the internal structure of the soil colloidal material remains unaltered. In his experiments alteration set in when the colloids were heated above 400° C.

Table 53. Heat of wetting of soil colloids at different moisture contents. (From Hoseh, 1937, Table 6)

Temperature (°C)	Altamont		Yolo		Vina		Aiken	
	Moisture left %	Heat of wetting (cal/g)	Moisture left %	Heat of wetting (cal/g)	Moisture left %	Heat of wetting (cal/g)	Moisture left %	Heat of wetting (cal/g)
Room	100.0	2.45	100.0	1.45	100.0	---	100.0	0.99
47	57.93	3.88	56.43	1.94	67.00	2.81	54.15	1.09
70	29.03	5.53	27.07	4.39	33.49	6.33	35.77	6.36
110	23.75	10.59	21.88	9.10	28.59	15.45	33.94	10.96
200	18.42	11.01	18.35	18.03	25.24	15.19	30.43	8.32
340	9.83	---	10.86	65.13	16.70	41.00	8.84	43.89
400	4.89	34.23	2.33	61.13	8.57	45.49	3.60	55.60
500	None	7.34	None	None	None	3.50	None	None

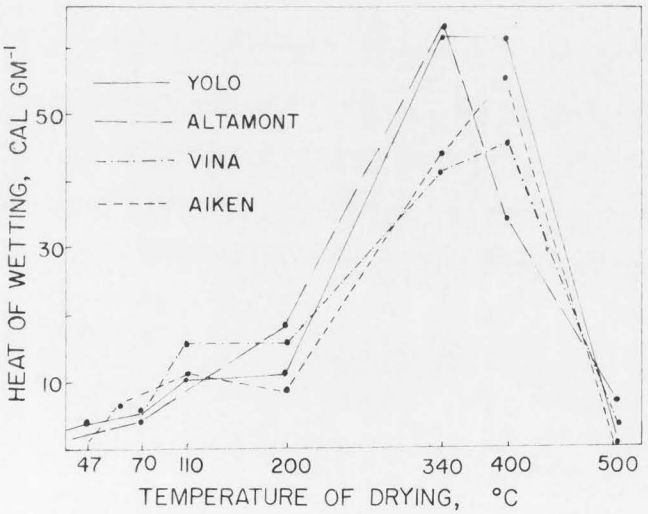

Figure 24. The heat of wetting of soil colloids dried at different temperatures. (From Hoseh, 1937, Figure 3)

Comments

The experimental data presented support the proposition that non-reproducible experimental results for heats of wetting, adsorption isotherms, and surface areas are associated with slight--sometimes very slight--differences in initial moisture contents. The results presented prompt certain observations: (i) Sample preparation results in changes which are themselves rate processes. Hence, unless the conditions of reaction are meticulously controlled, samples which have undergone varying extent of reaction are prepared. (ii) As the moisture content of porous solids decreases, smaller and smaller increments of moisture content change are associated with the same increments of change in surface or interfacial energy. A consequence is that moisture content is a very insensitive measurement of the reaction potential of "dry" porous materials. (iii) The natural variability of soils and other porous solids suggests the desirability of beginning with as homogeneous a raw material as possible.

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Proposition No. 2

The rate determining process for the approach to equilibrium in the case of adsorption of water on dry colloidal materials in vacuo is the dissipation of heat rather than the rate of condensation or uptake of water vapor, or

Little success can be expected in studying the kinetics of adsorption of moisture by soils using "high vacuum" technique.

Evidence A

Introduction. Our first evidence comes from a source which at first may appear quite foreign to the discussion, namely vapor pressure determination. In principle, one method of determining the vapor pressure of an unknown solution is to place it in a desiccator with a calibrated solution and let distillation occur until the vapor pressures are in equilibrium. (This is the so-called "isopiestic" method of vapor pressure determination.) At first thought one might expect that the rate of vapor diffusion limits the rate of approach to equilibrium. Sinclair (1933) examined the problem deeper, however, and concluded that the rate of heat transfer between the beaker where the vapor condenses to the one in which it evaporates is probably more often limiting.

Theory. The soundness of this argument rests on the facts that thermal equilibrium controls the vapor pressure equilibrium and that vapor diffusion is fast in vacuo. His reasoning is similar to the following:

i. As soon as air is removed in evacuation, the vapor pressure at the surface of all of the solutions is the same, but their temperatures are different. (The solutions have different wet-bulb temperatures at the same saturation vapor pressure.)

ii. At 25° C d(v.p.)/dT for water is 1.4 mm per degree. Hence 1/1.4 = .7 from which it is seen that for pure water a temperature difference of 0.7° C between two water surfaces means that the vapor pressures will differ by 1 mm Hg and cannot come to equilibrium until their temperatures do so.

iii. "The latent heat of vaporization of water at 25° C is 2436 joules per gram. Therefore, if we have two surfaces differing in temperature by 0.0007° C and separated by a medium of thermal conductance equivalent to one centimeter cube of the undermentioned materials, the times required for 1 gram of water to distil, or 2436 joules to flow, from one to the other may be calculated from the thermal conductivities (without convection) to be for (a) glass-10 years, (b) water-17 years, (c) gases-500 years, (d) mercury-15 months, (e) copper-10 days."

Taking the above considerations into account, Sinclair believed the isopiestic method might still be practical provided good thermal conduction were provided between the solutions and small quantities of solutions were used. "The factors limiting the rate of attainment of equilibrium would then be diffusion of solute and conduction of heat through the solutions."

Experimental. To test his ideas, Sinclair placed solutions of potassium chloride in silver-plated copper dishes "fitting neatly together" which rested on a copper base. These solutions approached identity of concentration at a feasible rate when rocked in an evacuated desiccator vessel in a thermostat. "Using about 2-cc. quantities of approximately 1 M potassium chloride, it was found that a 25 per cent difference could be reduced to 1 per cent in twenty-four hours."

Evidence B

The above discussion emphasizes the stringent temperature requirements in obtaining vapor pressure equilibrium of water. The next argument indicates the magnitude of temperature unbalance which can result when water is sorbed by colloidal materials. Again the evidence is from outside the field of soils. It is as follows:

Introduction. Two important properties of textile fibers are (a) the hygroscopic nature of the fibers and (b) their large surface:volume ratio. The first makes possible exchange of water vapor between the fibers and an air-water vapor atmosphere. If, for example, the radius of the average wool fiber is taken as 10 microns so that 1 cm^3 of wool fiber has a surface of roughly 2000 cm^2, the large surface:volume ratio suggests that even if diffusion determines the time required for the fibers to come to equilibrium with changed water vapor conditions, the time interval will be small. If the diffusion coefficient for water in keratin is taken as 10^{-5} cm^2 sec^{-1}, the time required for wool fiber to come within 80 per cent of its equilibrium value when water vapor conditions are changed, is roughly 10^{-2} sec. This rough calculation indicates that the rate of uptake per se may not be reaction rate controlling. Since adsorption and desorption are accompanied by comparatively large evolution and absorption of heat, we again realize the need of considering thermal effects.

Experimental. King and Cassie (1940) measured the rate of adsorption of water vapor by wool fibers when the complicating influences of diffusion and heat of adsorption were eliminated and allowed for, respectively. Diffusion of water vapor through any surrounding atmosphere was eliminated by making the adsorptions in vacuo. The temperature of the wool was studied by winding the sample (about 0.25 gm of merino wool silver) about a 16 cm length of No. 50 S.W.G. platinum wire employed as a resistance thermometer. The regain of the wool (the water content of the wool on the dry weight basis) was measured as the extension of a spiral spring. All measurements were made in an air thermostat maintained at 25 ± 0.2° C.

Results and Discussion. The results of the experiments are presented in Figures 25, 26, and 27. Figure 25 presents the kinetics of the adsorption process, i.e., the % regain as a function of time after water vapor was admitted to the sample. Figure 26 is the adsorption isotherm for water vapor on wool obtained by introducing increasing amounts of

water vapor into the adsorption chamber, and measuring the spring elongation and water vapor pressure after a time interval long enough for the wool to return to 25° C. This adsorption isotherm is clearly a Type II isotherm, the same as is observed for soil.

Figure 27 presents the temperature of the sample as a function of time after admitting water vapor into the adsorption chamber.

The discussion of the data is given in essentially the authors' own words as follows:

> The effect of the increase in temperature on regain of the fibres can be determined from the Kirchoff relation... which states that if regain is to remain unchanged, the temperature and pressure must be varied according to the relation:
>
> $$\ln (p/p_o) = Q/R(1/T_o - 1/T) \qquad (1)$$
>
> where q is the heat of absorption per gm. of water vapour and c is the specific heat per gm. of wool.
>
> Now, q is large, being roughly 750 cal./g. for dry wool (cf. Hedges, 1926), and c is 0.3 cal./g./°C... and according to equation (1) a large water vapour pressure will be required to give the sudden increase of regain to 2% even when the fibres reach equilibrium with the water vapour instantaneously. Under the conditions of the experiment just described, the wool was originally at 25° C and water vapour at 23.5 mm. was suddenly introduced. If the temperature of the wool remained at 25° C. its regain would be more than 30%. But rise of temperature, because of heat of absorption, makes the regain immediately acquired much less. This initial regain can actually be determined by assuming the wool to come instantaneously to equilibrium with any water vapour and temperature conditions. Table I shows the calculation.

Table I.--Regain and temperature of wool suddenly exposed to an increase in water vapour pressure from 0 to 23.5 mm at 25° C. T_o = 25° C. p = 23.5 mm.

p_o, mm.	M, %	T, °C	$\frac{q}{c} \times \frac{M}{100}$, °C.	$(T_o + \Delta T)$, °C.
0.235	1.2	104	30	55
0.470	2.0	89	50	75
0.705	2.4	81	60	85

Column (1) contains water vapour pressures arbitrarily chosen to cover likely values. The second column gives the

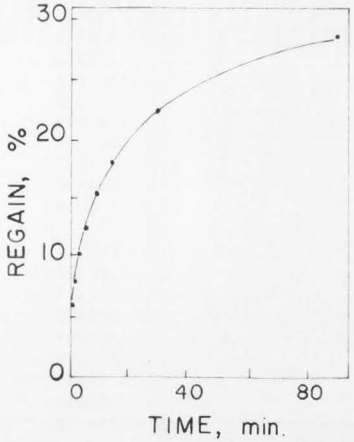

Figure 25. The increase in weight of the wool sample as a function of time of adsorption.

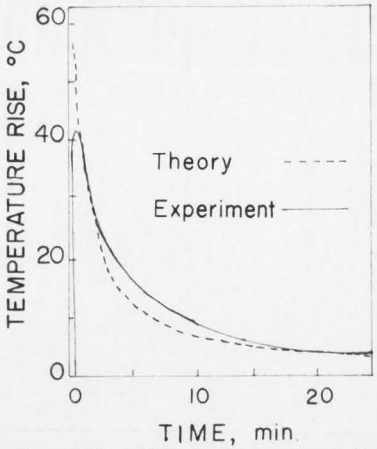

Figure 27. Temperature rise of the wool as a function of absorbing time.

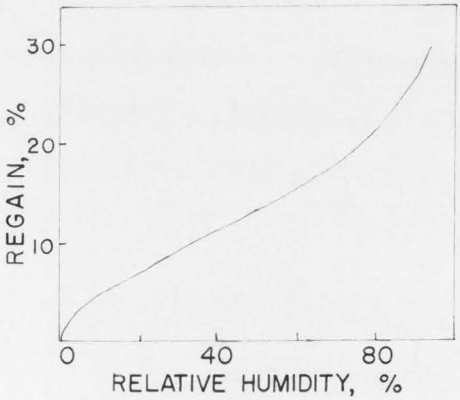

Figure 26. Adsorption isotherm of water vapor on wool.

regains corresponding to these pressures at 25° C.; they are obtained from the experimental curve shown in Fig. 2. T is obtained from Kirchoff's relation with p equal to 23.5 mm.; it is the temperature giving equilibrium with the regain of column (2) for p equal to 23.5 mm. The fourth column is obtained from equation (2). The regain first acquired by the wool when water vapour is introduced will be approximately that where T equals $(T_o + \Delta T)$; interpolation in Table I gives a value of roughly 2.3%. Hence, even though the conditions of the experiment were such that a regain of more than 30% would be ultimately acquired by the wool, it cannot because of heat of absorption increase instantaneously by more than 2.3%.

The instantaneous increase of regain on opening the inlet tap cannot be accurately determined from the graph of Fig. 1. The first observed point is 15 sec. after introducing the water vapour, and at this time the regain is nearly 4%. The time required for the fibres to come to equilibrium with the water vapour-temperature conditions in their immediate neighbourhood must, therefore, be considerably less than 15 sec.; how much less, it is impossible to estimate.

Table I shows that the temperature of the wool should rise to roughly 80° C. Experimental observations recorded on Fig. 3 do not give a point much higher than 65° C., but as this temperature was observed 30 sec. after introduction of the water vapour, considerable cooling has clearly taken place; a temperature of 80° C is not inconsistent with the cooling curve.

Conclusions. King and Cassie concluded that:
(1) Based on the assumption that the fibers are always in equilibrium with the atmosphere in their immediate neighborhood in such in vacuo experiments, the shapes of the regain-time curves are entirely due to the external factors of diffusion and dissipation of heat, and bear no relation to the diffusion of water into the fibers.
(2) Little quantitative data were obtainable in this experiment on the rate of pickup of water vapor except that the time to approach equilibrium must be less than 15 sec.
(3) The time required for the fibers to come to equilibrium with any change in conditions can be wholly neglected compared with the time required for dissipation of heat or diffusion of water vapor.
(4) Contrary to many previous deductions in various publications, nothing can be learned of the surface structure of fiber colloids from the study of regain-time curves.

Implications and Applications. The above conclusions may not be generally applicable but any researcher doing work on either adsorption or desorption should be aware of these ideas. The consequences of the existence

and the mechanisms of dissipation of the heats of adsorption and desorption seem especially to be neglected by researchers. If, for instance, a worker is studying the adsorption of a rather volatile material the initial temperature increase would greatly accelerate the desorption process. Such an effect would emphasize the difference between the number of molecules being adsorbed and the number evaporating, i.e., the net reaction.

Another implication of these results is that many sorption experiments reported as isothermal experiments have, in fact, not been. This suggests that reported thermodynamic functions such as enthalpy of adsorption obtained from the equation

$$\log p = (\Delta H_{ads}/2.303R)1/T + C,$$

where C is a constant and the other terms have been previously defined, must be in error. Any such error would then be inherent in entropy and free energy calculations involving ΔH_{ads}.

If regain-time curves are merely cooling curves, i.e., they reflect increased adsorption as temperature decreases, one must beware of interpretations of apparent slow rates of adsorption and desorption in terms of surface forces.

In careful kinetic studies the experimenter will have to give careful attention to the measurement of time.

It is not known whether these results hold for soil or not since no reports could be found in the literature in which data for adsorption or desorption of water on soil or clay minerals had been interpreted in light of the possibility of these pronounced thermal effects. There are numerous results in which the regain-time curves and adsorption isotherms are the same as those presented by King and Cassie for wool, however.

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